# PHASE EQUILIBRIA & DIAGRAMS

(NOT interesting for polymers)

→ many identical "things" JOIN together creating PHASES! (atoms, molecules)

PHASE = A CHEMICALLY & STRUCTURALLY HOMOGENEOUS REGION OF THE MATERIAL

→ if I change T, P, or composition, it can happen that the PHASE OF A SYSTEM CHANGES!

⇒ I NEED TO PLOT A "PHASE DIAGRAM" to describe such behavior

→ we show PHASE DIAGRAMS @ EQUILIBRIUM, therefore we DO NOT REPRESENT SUPERHEATED solids & SUPERCOOLED LIQUIDS!

→ COMPONENTS OF A PHASE

"the CHEMICALLY DISTINCT & ESSENTIALLY INDIVISIBLE SUBSTANCE"

EXAMPLE • take PURE Al

PURE Al ⇒ forms FCC structure

⇒ 1 COMPONENT (Al) @ 1 PHASE (SOLID FCC)

• TAKE ICE, add Water (liquid)

⇒ 1 component ($H_2O$) & 2 PHASES (SOLID ICE) + (LIQUID WATER)

• take COPPER, is FCC, take Ni, is FCC

Cu + Ni mixed together FORM

a random solution of Cu & Ni ⇒ SOLID SOLUTION

2 components (Cu) + (Ni) & 1 PHASE (SOLID SOLUTION random FCC)

• Window's glass

$SiO_2 + Na_2O + CaO$ → 3 components ($SiO_2$) + ($Na_2O$) + ($CaO$)

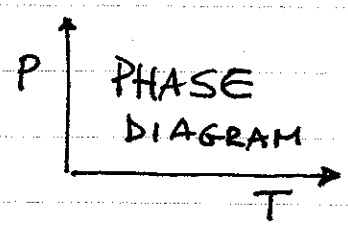
& 1 PHASE (amorphous)!

PE 1

# ONE COMPONENT SYSTEM

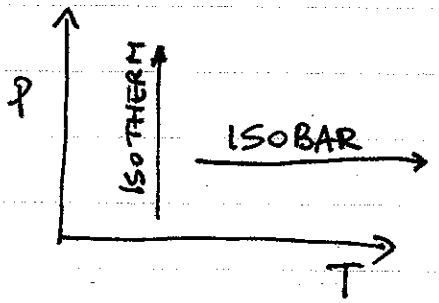
WHAT can I change ? P, T, Comp (No) ⇒ P & T only

how many degrees of freedom ? 2 ⇒




const P = ISOBARS (V const ISOCORES)

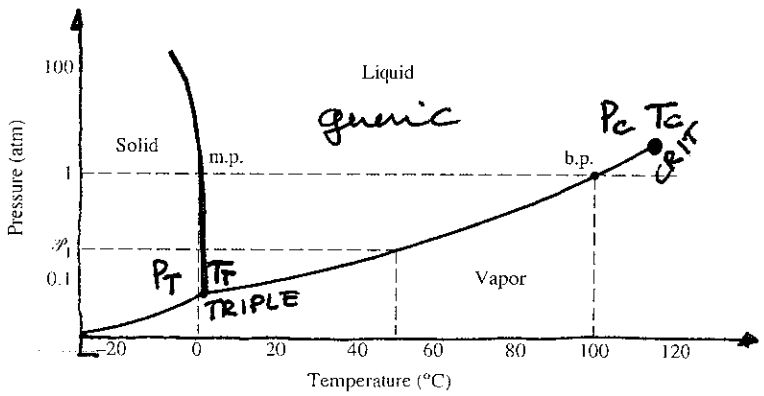
const T = ~~cccccc~~ ISOTHERMS




ONE COMPONENT PHASE DIAGRAM

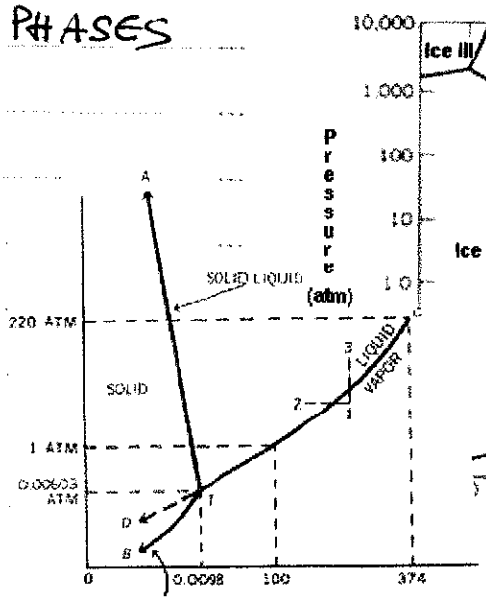
LINES = PHASES BOUDARIES

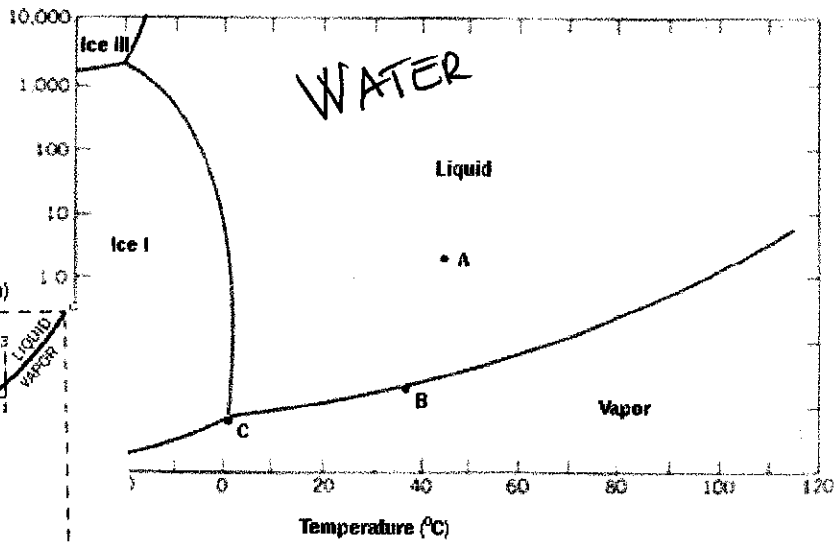
REGIONS = PHASES




$T_T, P_T$
TRIPLE POINT
SOLID & LIQUID & VAPOUR COEXIST

$T_c, P_c$
CRITICAL POINT
LIQUID & VAPOUR BECOME A SIMILAR FLUID




PE2

# GIBBS PHASE RULE

at Equilibrium

connects the $F$ = # number of degrees of freedom (things that we can change)

with $C$ = # of components

with $P$ = # of coexisting phases:

with 2 = # of state variables (things that we wish to change)

$P, T$

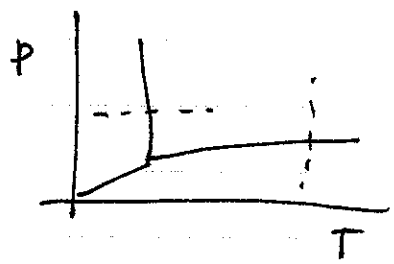
$$F = C - P + 2$$

(if $P$ is Fixed $\Rightarrow$ $F = C - P + 1$)

Example: Pick $H_2O$ with water liquid and ice

$\Rightarrow$ $C = 1$ $P = 2$

$F = 1 - 2 + 2 = 1$ $\Rightarrow$ to have 2 phases I can change only one variable T OR P,

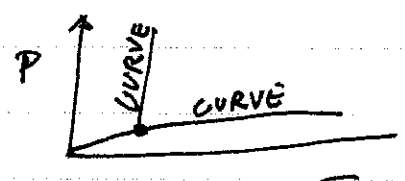



↓

IF I change P, T will follow T(P).

IF I change T, P will follow P(T)

$\Rightarrow$ coexistence of 2 phases, with 1 component leads to a curve 1 DIMENSIONAL T(P) OR P(T)!!




LOCUS

↑

need only 1 coordinate to describe!

PE3

2nd Example: Pick $H_2O$ ~~at~~ when ICE, LIQUID, VAPOUR coexist $\Rightarrow$ $C = 1$ $P = 3$

$$F = 1 - 3 + 2 = 0$$

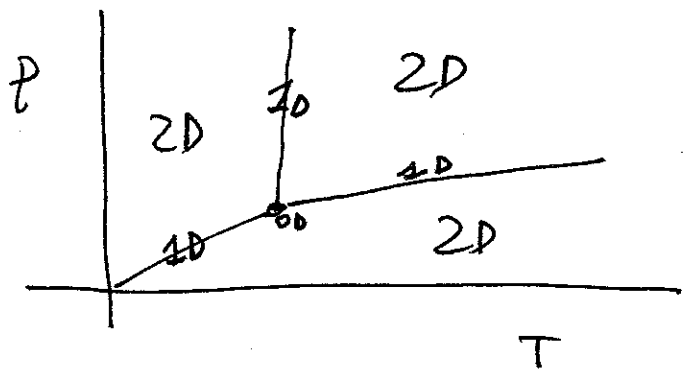
$\Rightarrow$ triple point is a ODimensional ~~do~~ ~~Do~~ LOCUS

OD = NO FREEDOM = <u>INVARIANT</u> $\Rightarrow$ A POINT

3rd Example: Pick $H_2O$ vapour $\Rightarrow$ $C = 1$ $P = 1$

$$F = 1 - 1 + 2 = 2$$

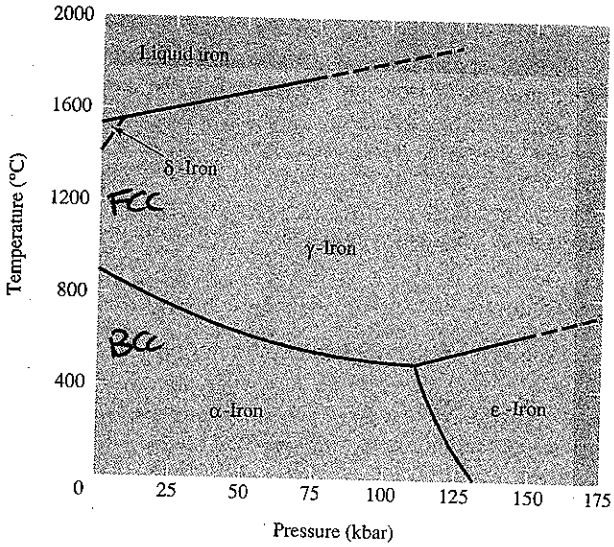
$\Rightarrow$ Vapour is a 2Dimensional LOCUS, a part of a plane with 2 coordinates to be described $\Rightarrow$ A REGION

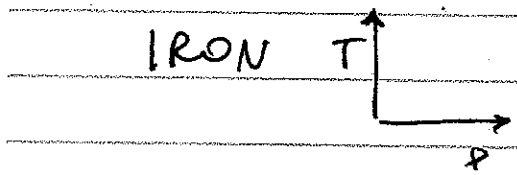


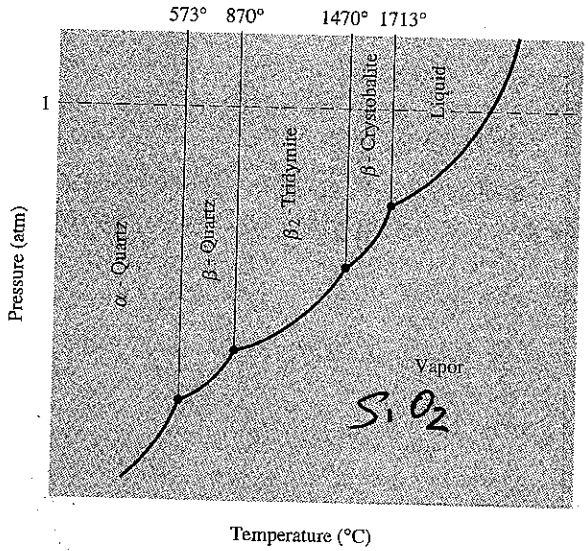

DIMENSION OF THE LOCI

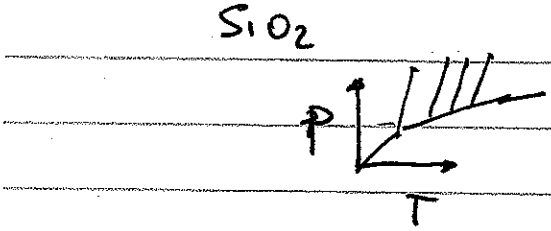
PE4

# MORE COMPEX ONE-COMPONENT SYSTEMS




PE5

# TWO-COMPONENT SYSTEMS

~~We~~ can change another variable C!! concentration of A or B in a MIX of A & B!!

$C_A$ ? Weight or ATOMIC ? (mass weight) (# atoms)

EXAMPLE

$C_H^a(H_2O) = \frac{2}{2+1} = 2/3$

$C_H^w(H_2O) = \frac{2}{2+16} = \frac{1}{9}$

Concentrations

WEIGHT ⇒ ATOMIC

$$C_A^{at} = \frac{C_A^w / W_A^{at}}{C_A^w/W_A^{at} + C_B^w/W_B^{at}} \quad [\text{in } 100\%]$$

$$C_A^{at} + C_B^{at} = 1$$

$W_A^{at}$ & $W_B^{at}$ atomic weight of A & B

$C_A^{at}$ & $C_B^{at}$ atomic concentrations

$C_A^w$ & $C_B^w$ weight concentrations

ATOMIC ⇒ WEIGHT

$$C_A^w = \frac{C_A^{at} * W_A^{at}}{C_A^{at} * W_A^{at} + C_B^{at} * W_B^{at}} \quad [\text{in } 100\%]$$

$$C_A^w + C_B^w = 1.$$

MOLAR mix $n_A$ MOLES of A & $n_B$ moles of B

$$N_A = n_A/(n_A+n_B) \quad \& \quad N_B = n_B/(n_A+n_B)$$

$$N_A + N_B = 1$$

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- SOLUBILITY

Put sugar in Water = solute & solvent

$T \uparrow C^{MAX} \uparrow$

$T \downarrow C^{MAX} \downarrow$

if $C_{sugar} \leq C_{sugar}^{MAX}$ ⇒ sugar does not precipitate

$C_{SUGAR}^{MAX}(T)$ = SOLUBILITY LINE → most solute without precipitation

PE6

SIMPLEST CASE

# 2-COMPONENTS SYSTEM A&B

# ISOMORPHOUS DIAGRAM FOR IDEAL

DEFINITIONS

ISOMORPHOUS = if you MIX A & B, at low temperature they form a SOLID-SOLUTION

When SOLID-SOLUTIONS? when A & B similar!!

HUME-ROTHERY RULES:

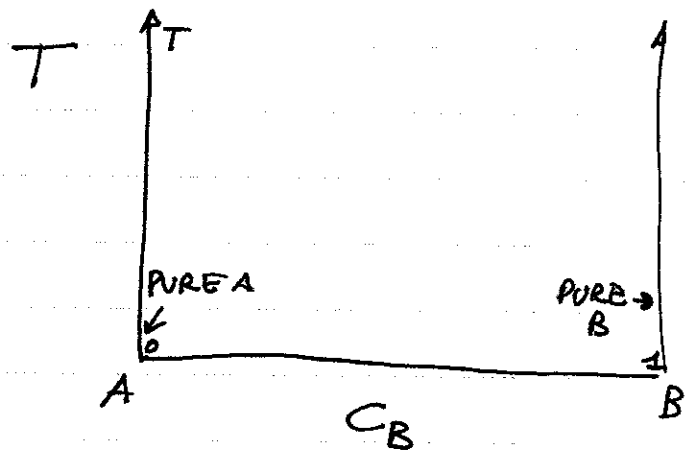
ISOMORPHOUS ⇐
1) SIZE A & B off of MAX 15%
2) ELECTRONEGATIVITIES ARE COMPARABLE
3) VALENCES ARE SIMILAR
4) CRYSTAL STRUCTURE OF PURE A & B IS IDENTICAL

EX Cu+Ni form A SOLID-SOLUTION = RANDOM MIX OF A & B WITH A STRUCTURE

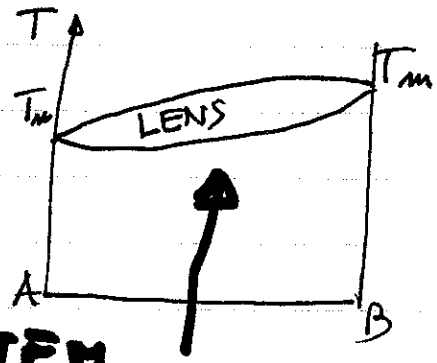
Cu ≃ Ni : they are ISOMORPHOUS

CONSTANT Pressure (1 ATM)

DRAW COMPOSITION DIAGRAM



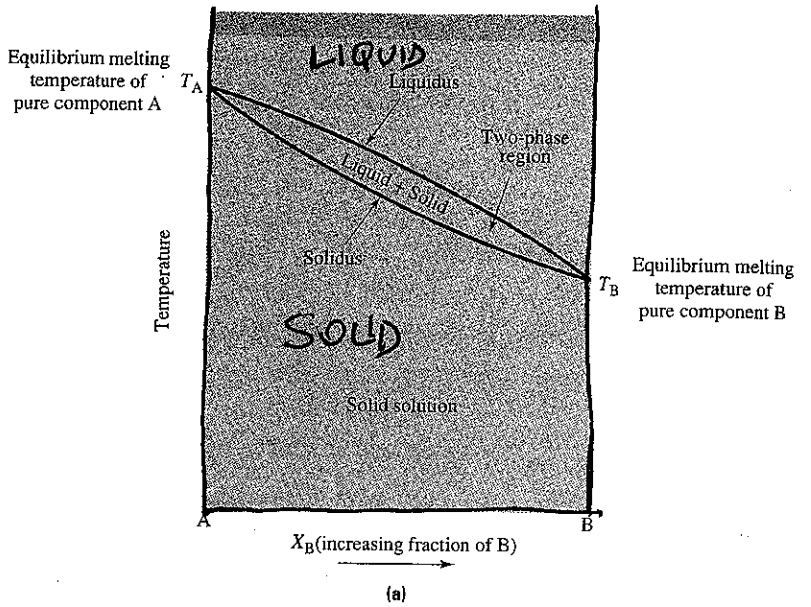

SUPPOSE $T_m(A) < T_m(B)$

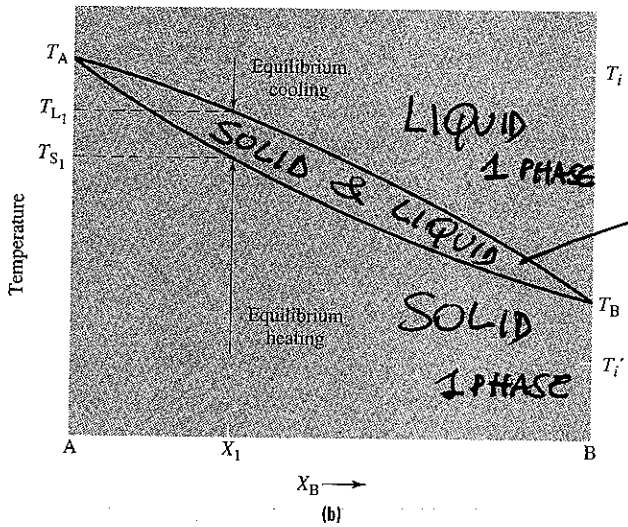



IDEAL LENS SYSTEM

PE7

**FIGURE 7.3–1**
The idealized binary (A-B) isomorphous system: **(a)** the composition-temperature phase diagram with associated definitions, and **(b)** a similar diagram showing the liquidus and solidus temperatures for a specific alloy of composition $X_1$.




IDEAL SYSTEM = ~~ISOMO~~ SOLID SOLUTION + LENS

P=cost ⇒ F=C−P+1

WHY? ORIGIN IS GIBBS RULE

~~COEXISTENCE~~

LOOK FOR TWO PHASE ~~REGIONS~~ OR

PURE A (OR B)

L C=1 F = 1 − 2 + 1 = 0

⇒ POINT @ 2 PHASES COEXISTING HAS NO ~~FREEDOM~~

⇒ POINT ⇒ $T_m(A)$

MIX A+B → C=2

F = 2 − 2 + 1 = 1 ⇒

THERE IS AN INTERVAL ($\Delta T$) FOR WHICH 2 PHASES COEXIST!

PE8

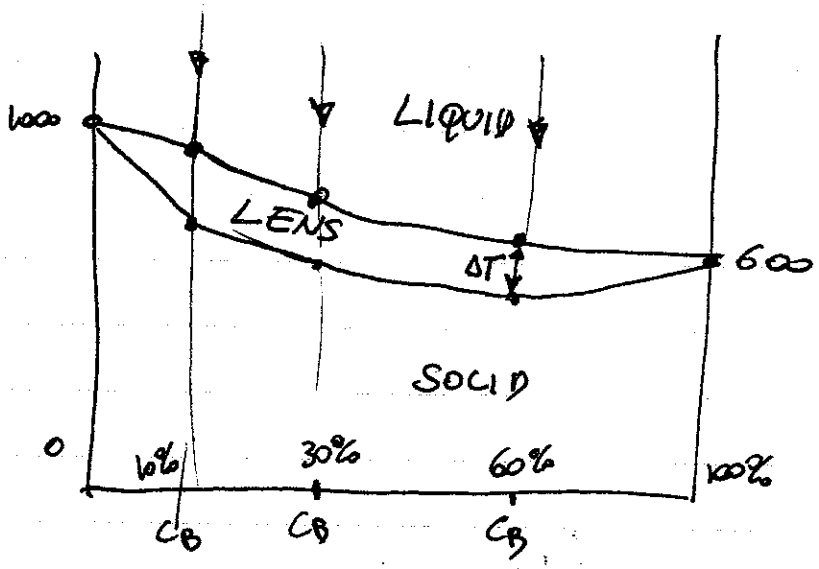
MEASUREMENT SCHEME  PURE A  $T_m(A) = 1000\,K$

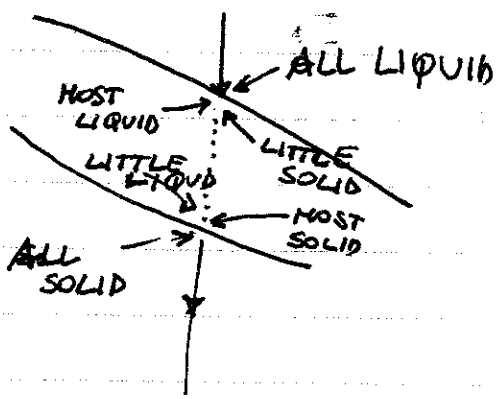
Mix A & B  $C_B = 10\%$ $\Longrightarrow$ 2 PHASE INTERVAL $[900, 700]\,K$

$C_B = 30\%$ $\Longrightarrow$ 2 PHASE INTERVAL $[800, 600]\,K$

$C_B = 60\%$ 2 PHASE INTERVAL $[700, 500]\,K$

Pure B  $C_B = 100$ $\Longrightarrow$ $T_m =$ 2 PHASE POINT $600\,K$




PE9

# HOW MUCH LIQUID & SOLID AND WHICH COMPOSITION THEY HAVE?

Remember that you are at equilibrium (go up slowly in Temperature VERY SLOWLY)

INSIDE A 2-PHASES REGION which concentrations?

Pick concentration & Temperature of your MIX

(C,T) = STATE POINT

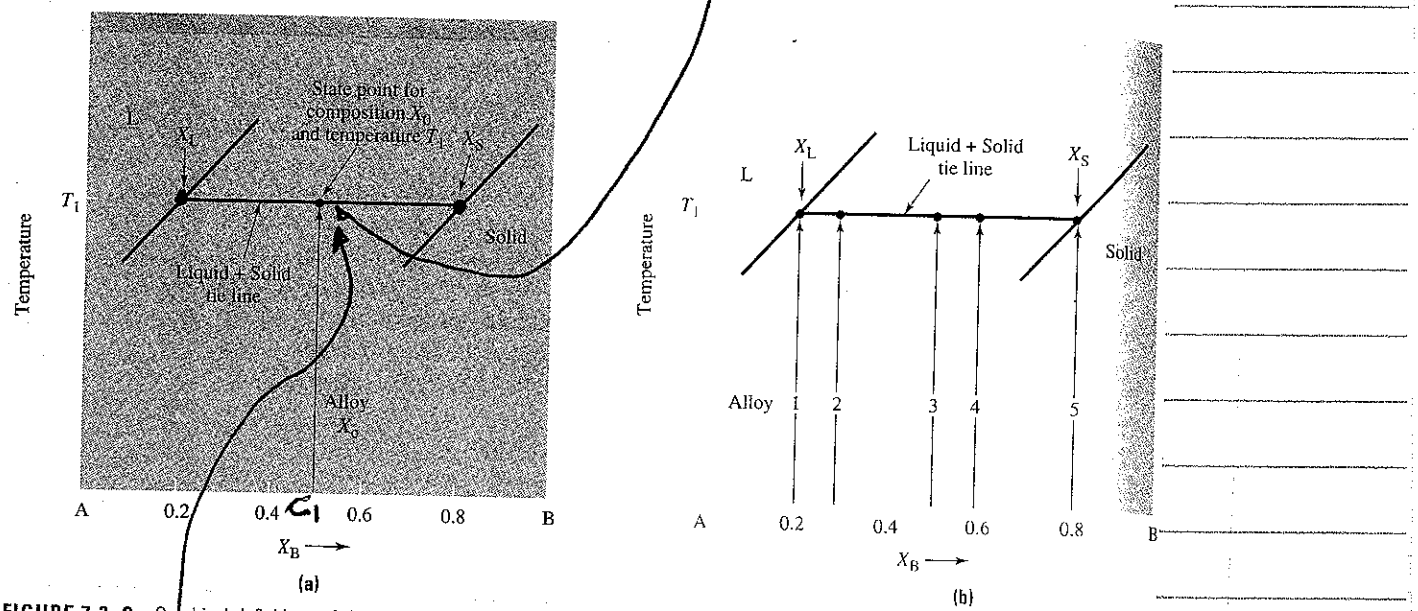



**FIGURE 7.3–2** Graphical definitions of the tie line and the lever rule in a two-phase field: **(a)** the tie line through the state point defined by temperature $T_1$ and alloy composition $X_0$, and **(b)** the same tie line shared by all five alloy compositions at temperature $T_1$.

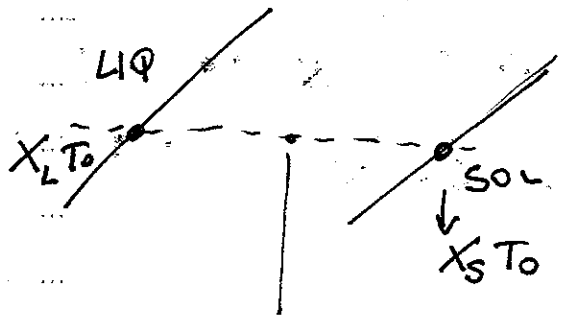
DRAW HORIZONTAL LINE

at $(T_1, C_1)$ then is TIE LINE

C or x (Book uses x so I use x but you should try to use c)

PEP

# LEVER RULE




$X$ = conc of B

$X_0 T_0 \Rightarrow$ Have $M_0$ mass
$\Rightarrow M_L$ is liquid @ conc $X_L$
$M_S$ is solid @ conc $X_S$

$\Rightarrow$ CONSERVATION OF MASS

CONSERVATION OF B

total mass of B = tot MASS B in LIQUID + tot B in MASS SOLID

$$M_0 X_0 = M_L X_L + M_S X_S$$

$$\Rightarrow X_0 = \left(\frac{M_S}{M_0}\right) X_S + \left(\frac{M_L}{M_0}\right) X_L$$

$$\Downarrow$$

$$X_0 = f_S X_S + f_L X_L$$

CONSERVATION OF TOTAL MASS

$$M_0 = M_L + M_S \Rightarrow 1 = f_L + f_S$$

$$\left.\begin{aligned} f_L + f_S &= 1 \\ f_S X_S + f_L X_L &= X_0 \end{aligned}\right\} \Rightarrow \begin{aligned} f_S X_S + (1 - f_S) X_L &= X_0 \\ f_S (X_S - X_L) &= X_0 - X_L \end{aligned}$$

Solutions But difficult ch remember TRY RULE

$$f_S = \frac{X_0 - X_L}{X_S - X_L} = \frac{X_L - X_S}{X_L - X_S}$$

$$f_L = \frac{X_0 - X_S}{X_L - X_S} = \frac{X_S - X_0}{X_S - X_L}$$

PE 11

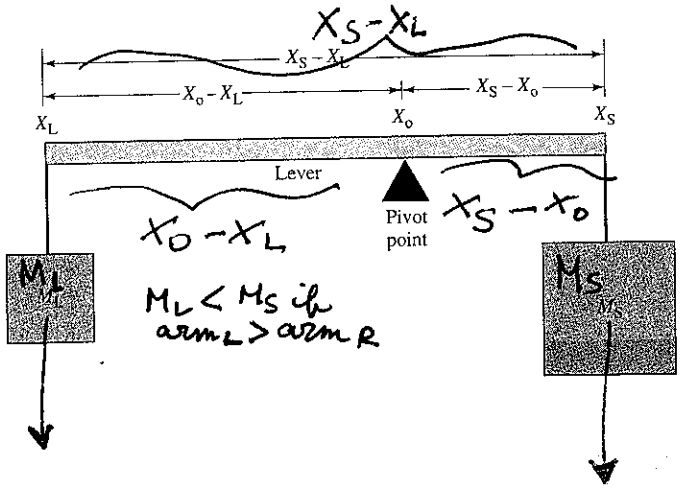



**FIGURE 7.3–3**
A schematic illustration of the lever rule. The tie line represents a "lever" with its pivot point located at the alloy composition $X_o$, its left end fixed at "position" $X_L$, and its right end located at $X_S$ with blocks of mass $M_L$ and $M_S$ resting on either end.

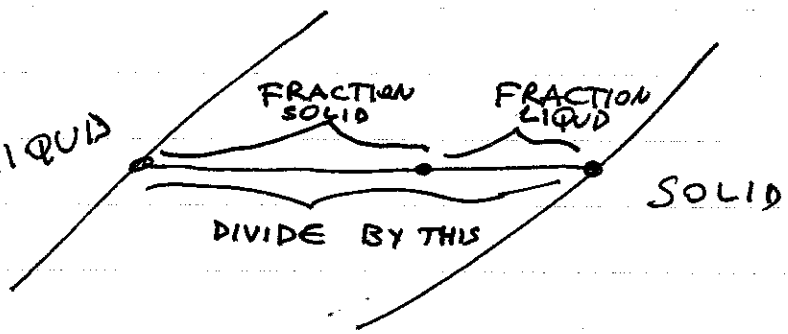
$M_S$ at the RIGHT depends on the LEFT part of the pivot

$$f_S = \frac{X_o - X_L}{X_S - X_L}$$

$M_L$ at the LEFT depends on the LEFT part of the pivot

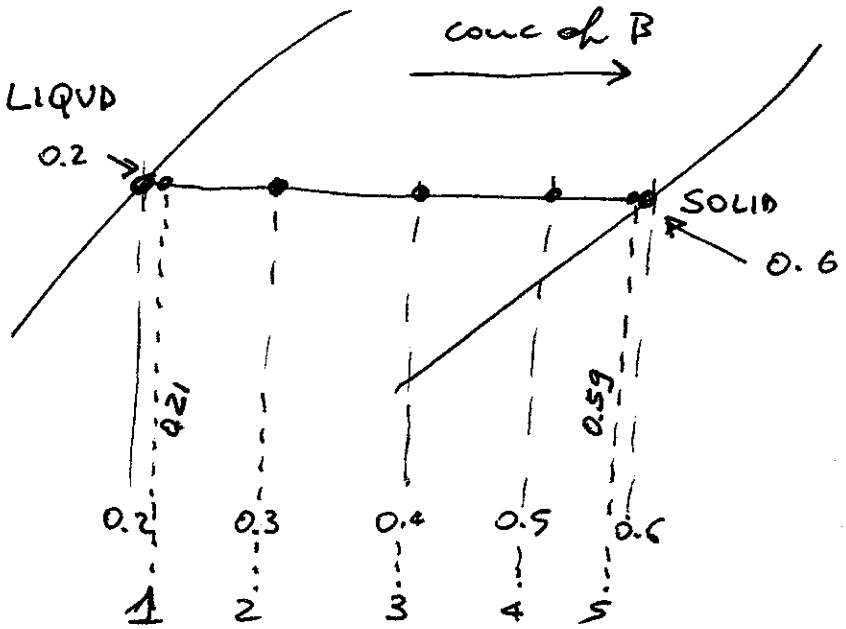
$$f_L = \frac{X_S - X_o}{X_S - X_L}$$

$\Rightarrow$




PE12

# EXAMPLE

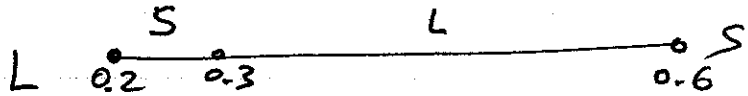



**Alloy 1**
~~$X_B$~~ $= 0.21$


$\Longrightarrow$ NORM $= 0.6 - 0.2 = 0.4$

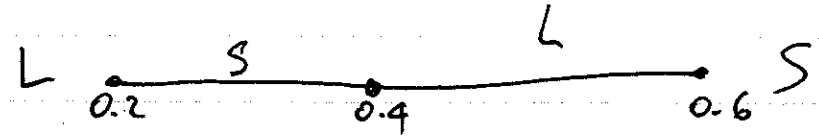
$f_S = \frac{0.21 - 0.2}{0.4} = 0.025$ $\quad f_L = 0.975$ almost ALL LIQUID

**Alloy 2**
$X_B = 0.3$



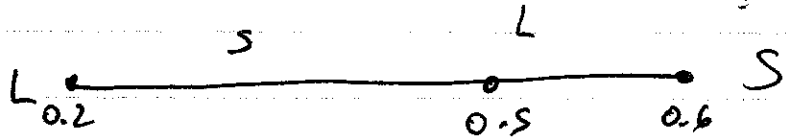

$f_S = \frac{0.3 - 0.2}{0.4} = 25\%$ $\quad f_L = 75\%$ Most liquid

**Alloy 3**
$X_B = 0.4$



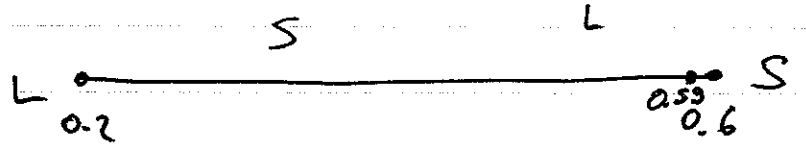

$f_L = \frac{0.4 - 0.2}{0.4} = 50\%$
$f_S = 50\%$

**Alloy 4**
$X_B = 0.5$




$f_L = \frac{0.5 - 0.2}{0.4} = 60\%$
$f_S = 40\%$

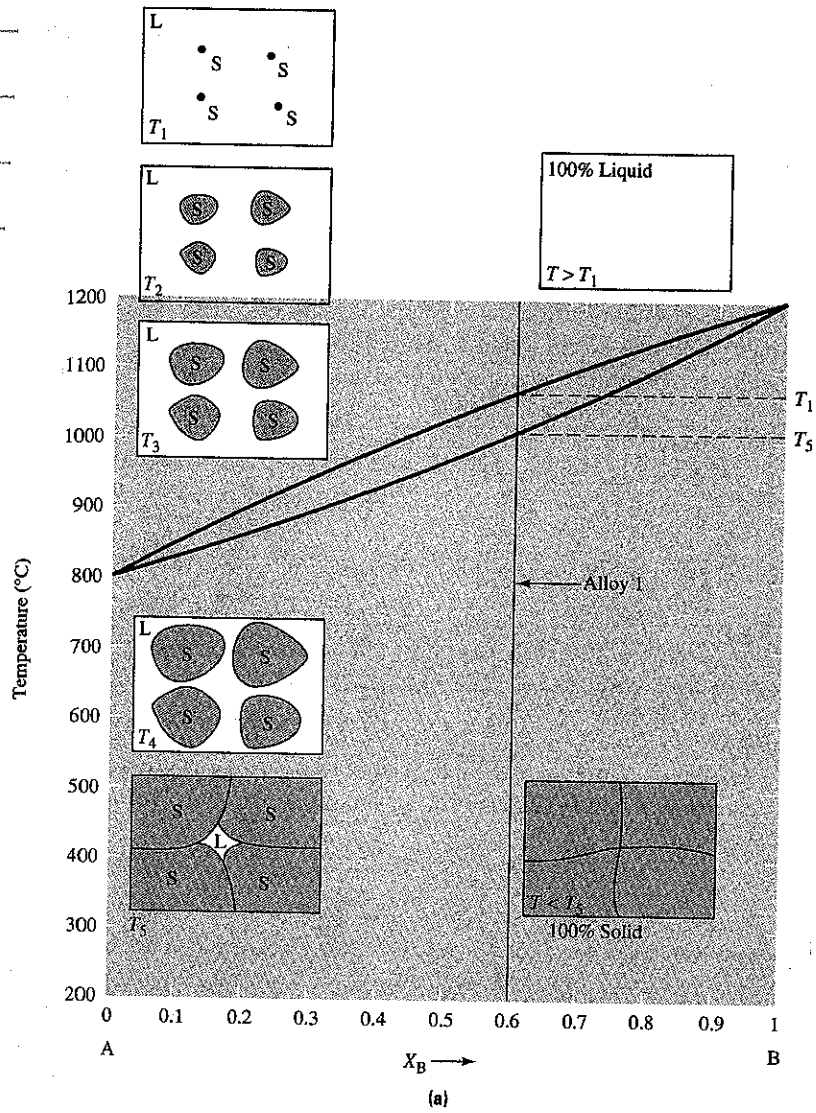
**Alloy 5**
$X_B = 0.59$




$f_L = \frac{0.59 - 0.2}{0.4} = 97.5\%$
$f_S = 2.5\%$
almost ALL LIQUID

PE13

# SOLIDIFICATION & MICROSTRUCTURE of an ISOMORPHOUS IDEAL ALLOY



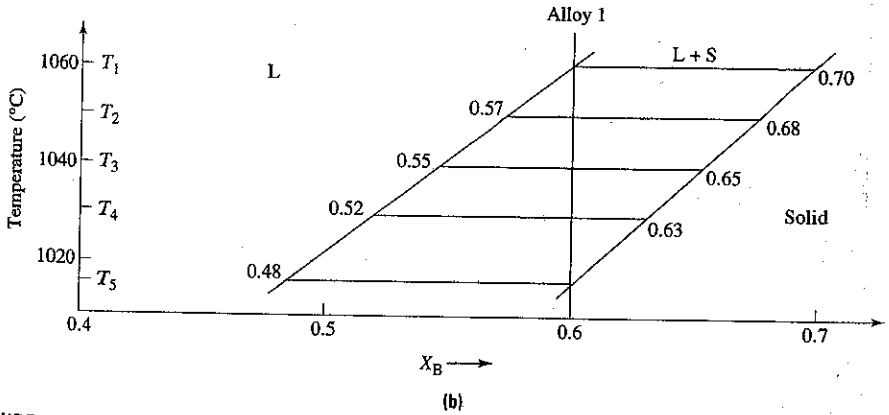
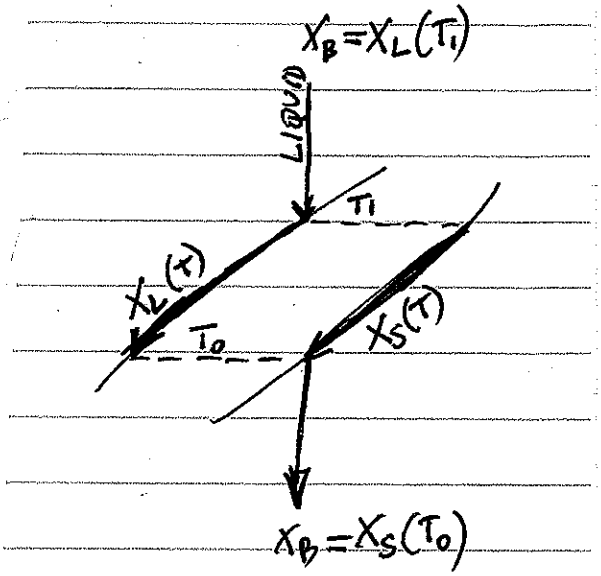
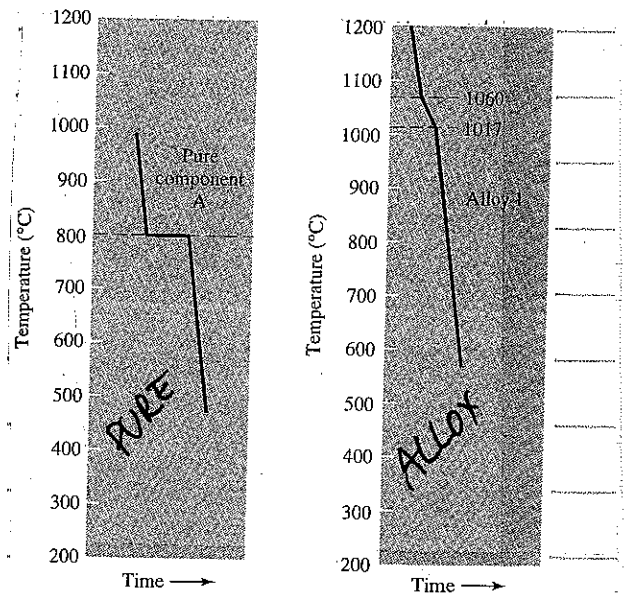



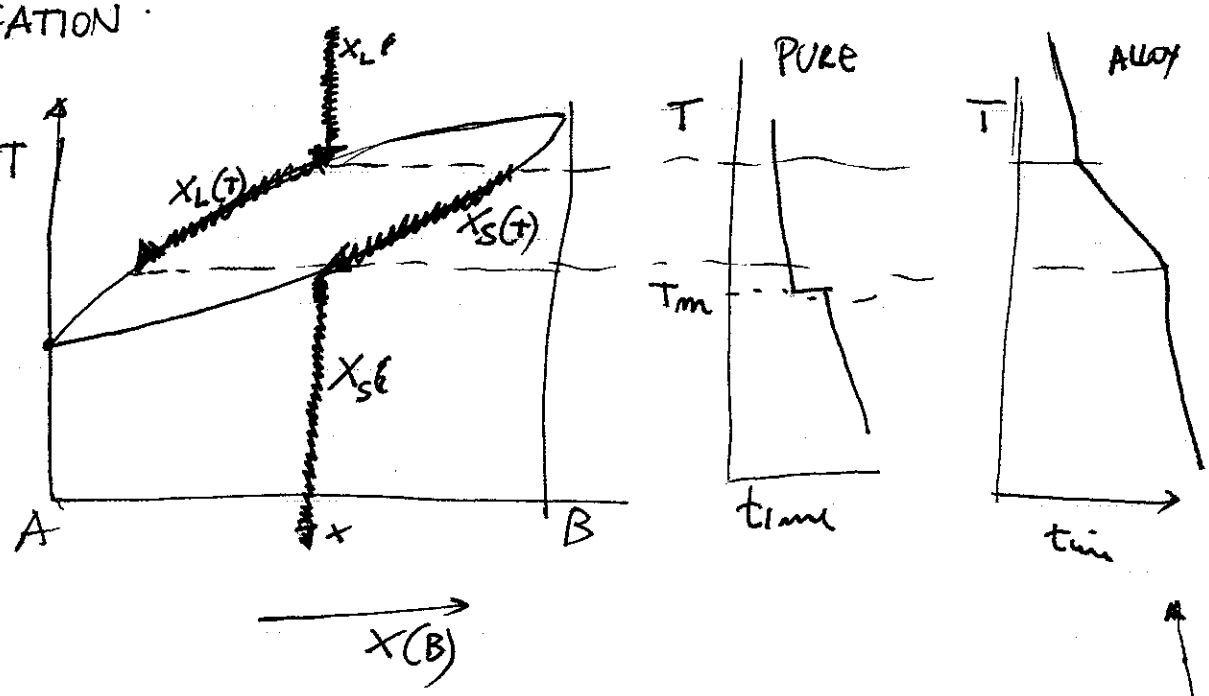

FIGURE 7.3–4 Equilibrium solidification of alloy 1 (composition 0.6 B): **(a)** the cooling path and sketches showing the development of the microstructure, and **(b)** an expanded section of part **(a)** showing the compositions of the liquidus and solidus boundaries in the range of 1010°C to 1060°C.




TIME TEMPERATURE PROFILE



SOLIDIFICATION




DETERMINATION: MIX, T↑, T↓ & WATCH LIQUID, SOLID

OR: T↓ and WATCH FOR HEAT FLOW OUT

ISOMORPHOUS SYSTEMS: FORM SOLID SOLUTION @ ALL OR TEMP.

Cu-Ni FCC

$NiO-MgO$ (Both NaCl) = FCC with basis one anion and one cation Ni OR Mg

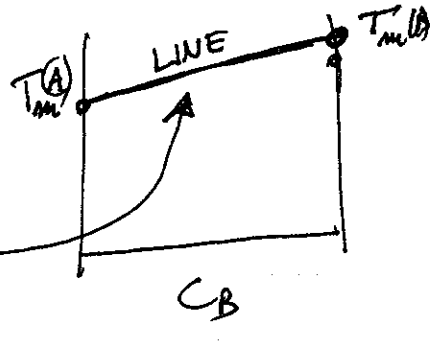
WHY I HAVE LENS ? Because of ENTROPY!

A–A Bond $E_{AA}$

B–B Bond $E_{BB}$

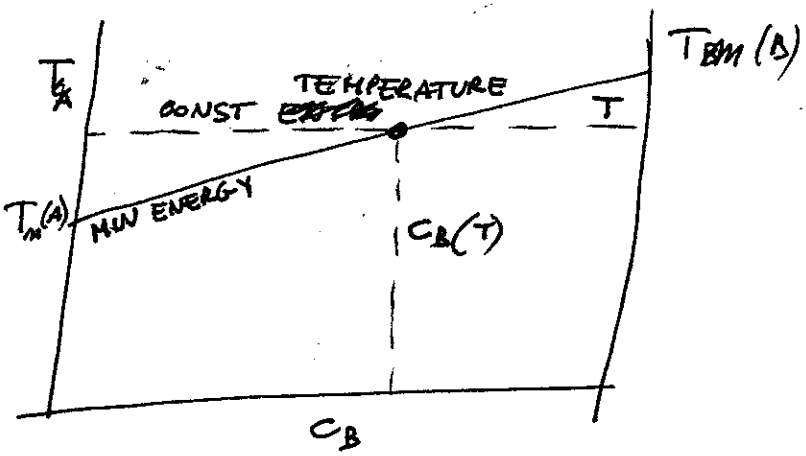
A–B Bond $E_{AB} = \frac{1}{2}(E_{AA}+E_{BB})$ IDEAL $\Rightarrow$

$\Longrightarrow$ MIN ENERGY




PE15

But remember THAT @ const P, & T we have to minimize $G = E + PV - TS$
have entropy effect




@ T $C_B(T)$ is ideal straight line $\Rightarrow$

$\rightarrow$ $x_B$ & $x_A = 1 - x_B$,

but have Temperature $\Rightarrow$ defects form $\Rightarrow$ some B are A & viceversa

$\Rightarrow$ $x_B \rightarrow x_B + \Delta x$ $\quad x_A \rightarrow x_A - \Delta x$

$\Rightarrow$ $\Delta x$ depends on energy required to form (with Arrhenius)

$\Rightarrow$ $S(\Delta x) = -k[(x_B + \Delta x)\log(x_B + \Delta x) + (x_A - \Delta x)\log(x_A - \Delta x)]$

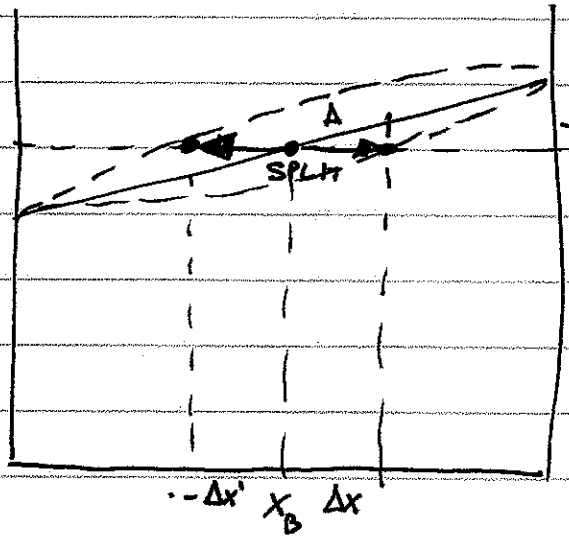
same way I have $x_B \rightarrow x_B - \Delta x'$ $\quad x_A \rightarrow x_A + \Delta x'$

$\Rightarrow S(\Delta x')$

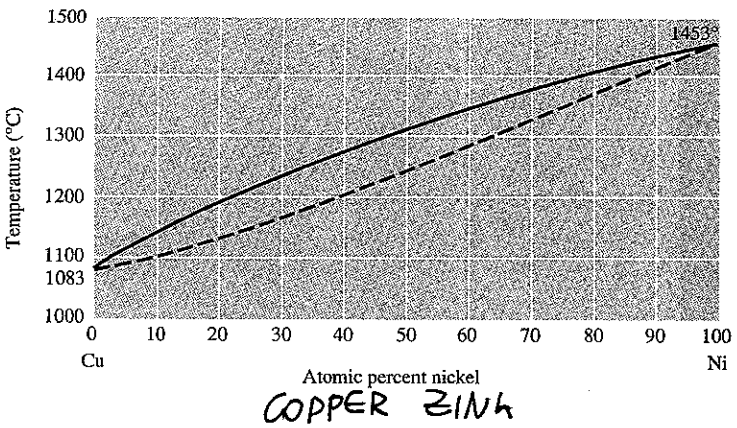
$\Delta x'$ depends on energy to form defect via ARRENIOUS

PE16 $\min\ [E + PV - T(S(\Delta x) - S(\Delta x'))]$

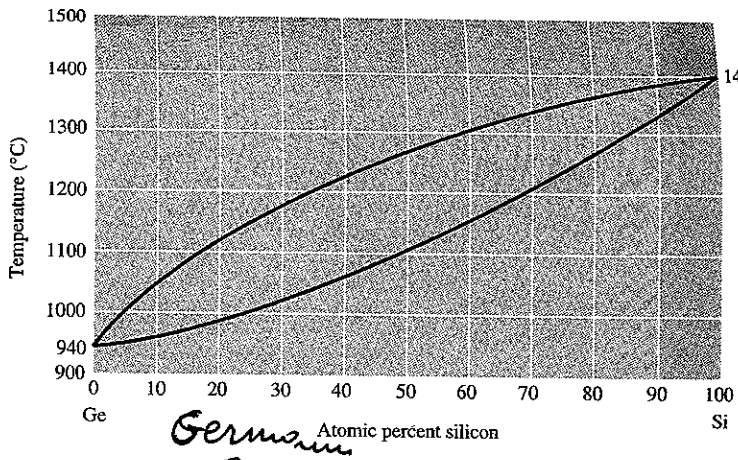
C



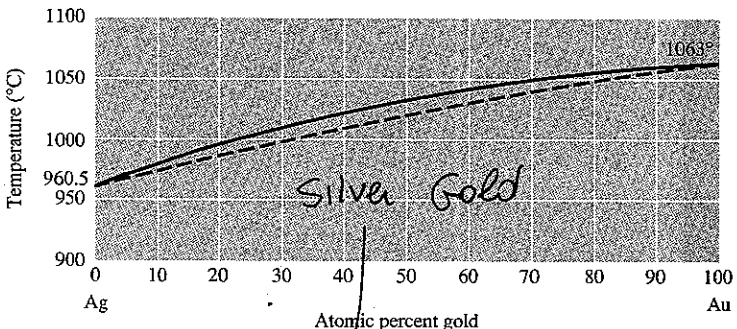

Temperature rules → ENTROPY ⇒ Formation of defects OR OFF-STOCHIOMETRY PHASES.




COPPER ZINK




Germanium Silicon




Silver - Gold

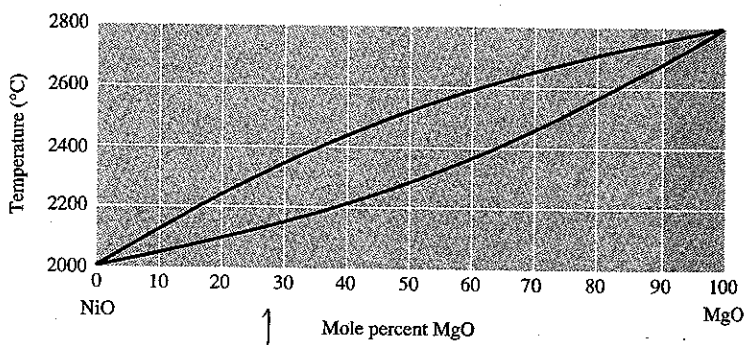



**FIGURE 7.3–6** Four binary isomorphous systems, Cu-Ni, Ge-Si, Ag-Au, and NiO-MgO.

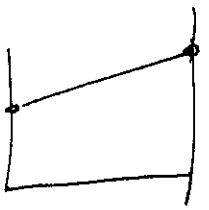
NICKEL-OXIDE + MAGNESIUM OXIDE

PE 17

through to have SOLID SOLUTION AT LOW TEMPERATURE (NO)

# DEVIATION FROM IDEALITY

- IDEAL $E_{AB} = \frac{1}{2}(E_{AA} + E_{BB})$ MIN(E) ⇒



Random

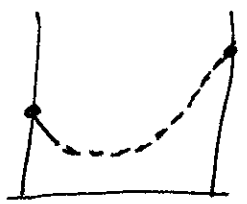
- CLUSTERING TENDENCY $E_{AB} > \frac{1}{2}(E_{AA} + E_{BB}) \Rightarrow E_{AB}$ is not "welcome" higher than ideal

it means that A prefers A to B & B prefers B to A! they do not want to mix too much in the solid phase


minimize # A-B Bonds

⇒ to minimize total energy temperature tries to destroy as soon as possible the solid phase

⇒ min(E)



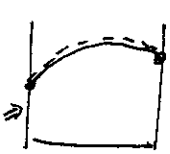
- ORDERING TENDENCY $E_{AB} < \frac{1}{2}(E_{AA} + E_{AB}) \Rightarrow E_{AB}$ is "welcome" lower than ideal

it means that A prefers B to A & B prefers A to B!

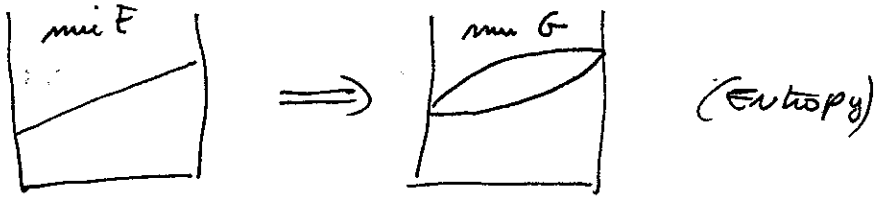
maximize # of A-B bonds

They WANT to mix and they resist to temperature (disorder) as much as possible!

PE18 ⇒ Temperature needs to work hard to destroy ordering! ⇒ min(E) ⇒

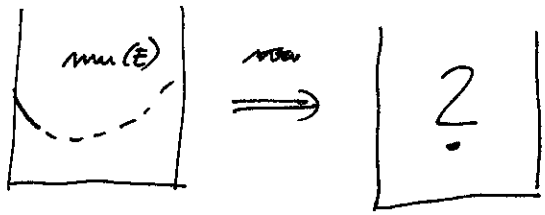


NOW IDEAL

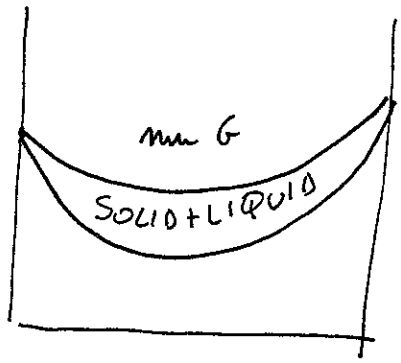



(Entropy)

CLUSTERING TENDENCE $E_{AB} > \frac{E_{AA} + E_{BB}}{2}$

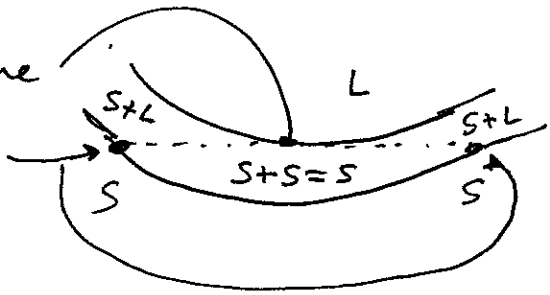



CAN BE A "BANANA"

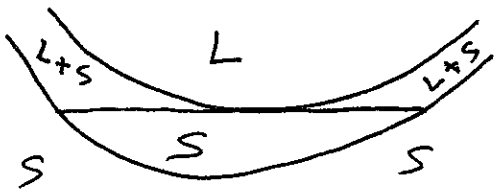



? No

because here I would split it therefore the lower part would be just SOLID



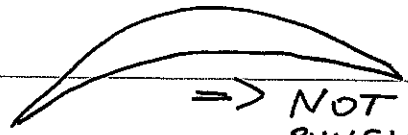

"BANANA" LENS DOES NOT EXIST!!




PE19

# CONGRUENT MELTING

SAME FOR ORDERING



⇒ NOT PHYSICAL

⇒ the LIQUIDUS & SOLIDUS must "touch" at the min AND max

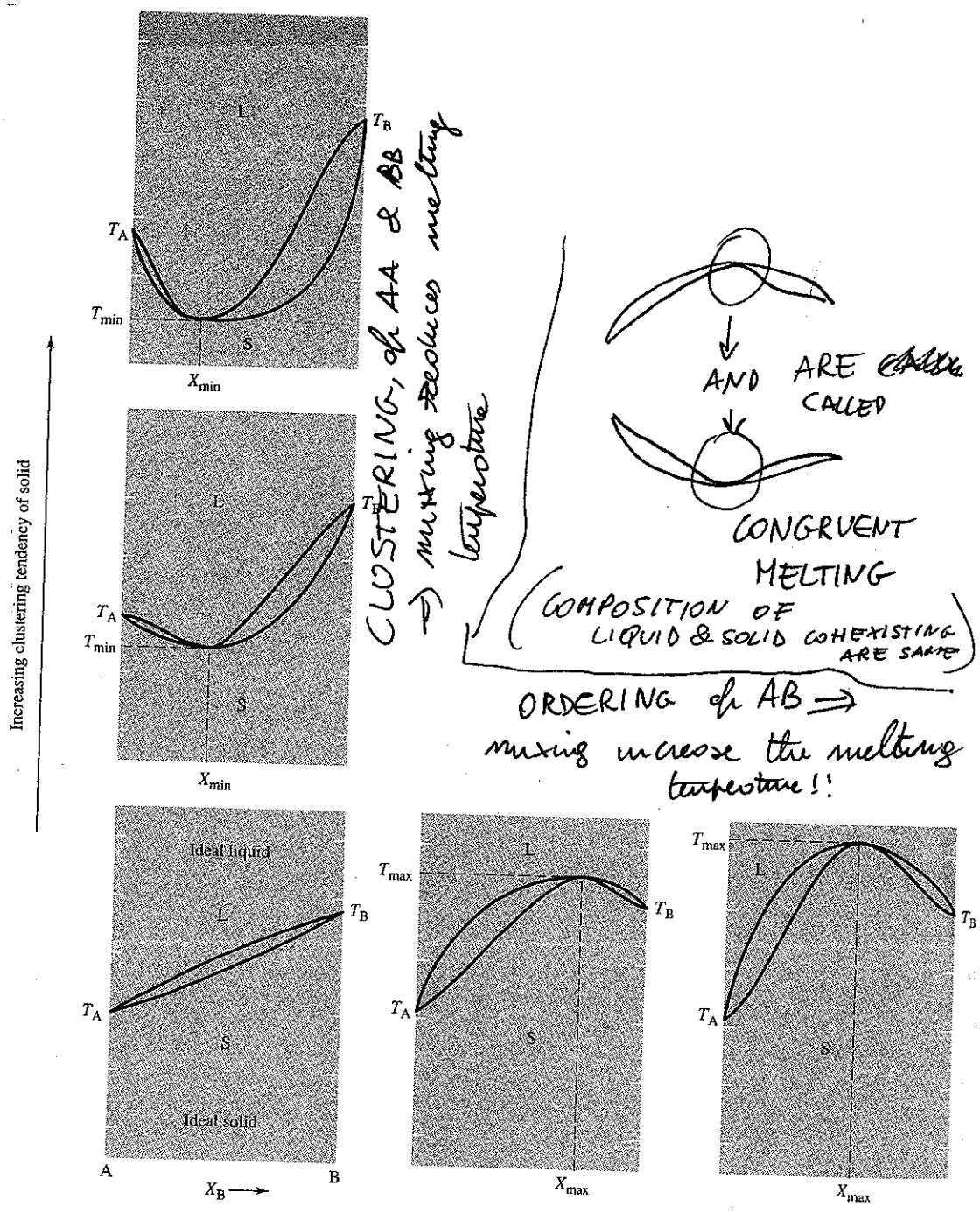



**FIGURE 7.3–7** Progressive change in the form of the isomorphous phase diagram as the solid and liquid phases deviate from ideal behavior.

PEP

AT ~~eutectic~~ CONGRUENT MELTING POINT
THE ALLOY SOLIDIFIES/MELTS ~~AT A~~ AT A GIVEN
TEMPERATURE ($T_{m(c)}$) AND CONCENTRATION (C)
AND NOT IN A TEMPERATURE INTERVAL

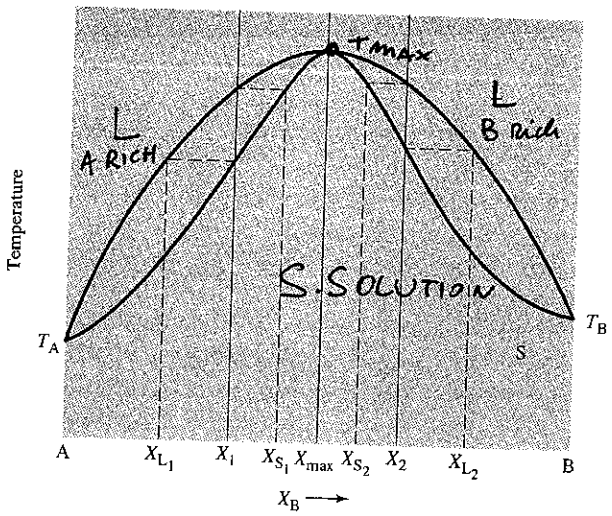



**FIGURE 7.3–8**
A binary phase diagram showing a congruently melting alloy of composition $X_{max}$. Two additional alloy compositions are shown.

IF YOU WANT TO MAKE AN ALLOY WHICH
RESISTS AT HIGHER TEMPERATURE THAN THE
CONSTITUENTS, THAN YOU NEED SOMETHING LIKE THIS

PLANES
ENGINES

IF YOU WANT TO MAKE AN ALLOY WHICH
MELTS AT LOWER TEMPERATURE THAN THE
CONSTITUENTS, THAN YOU NEED SOMETHING LIKE THIS

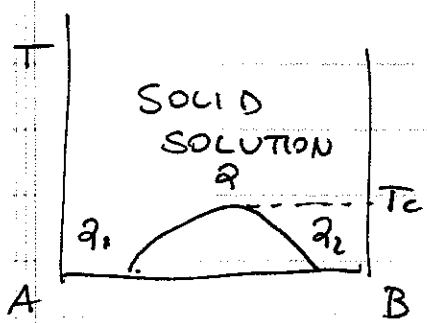
WELDING
SOLDERING
CAST

PE21

# EUTECTIC PHASE DIAGRAM

if CLUSTERING (A likes A better than B)
than at low Temperature the two elements do not mix well and and solid solution disappear

⇒




$\alpha$ = solid solution above $T_c$ (critical)

$\alpha_1$ = solid solution A-Rich

$\alpha_2$ = solid solution B-Rich

depending on the

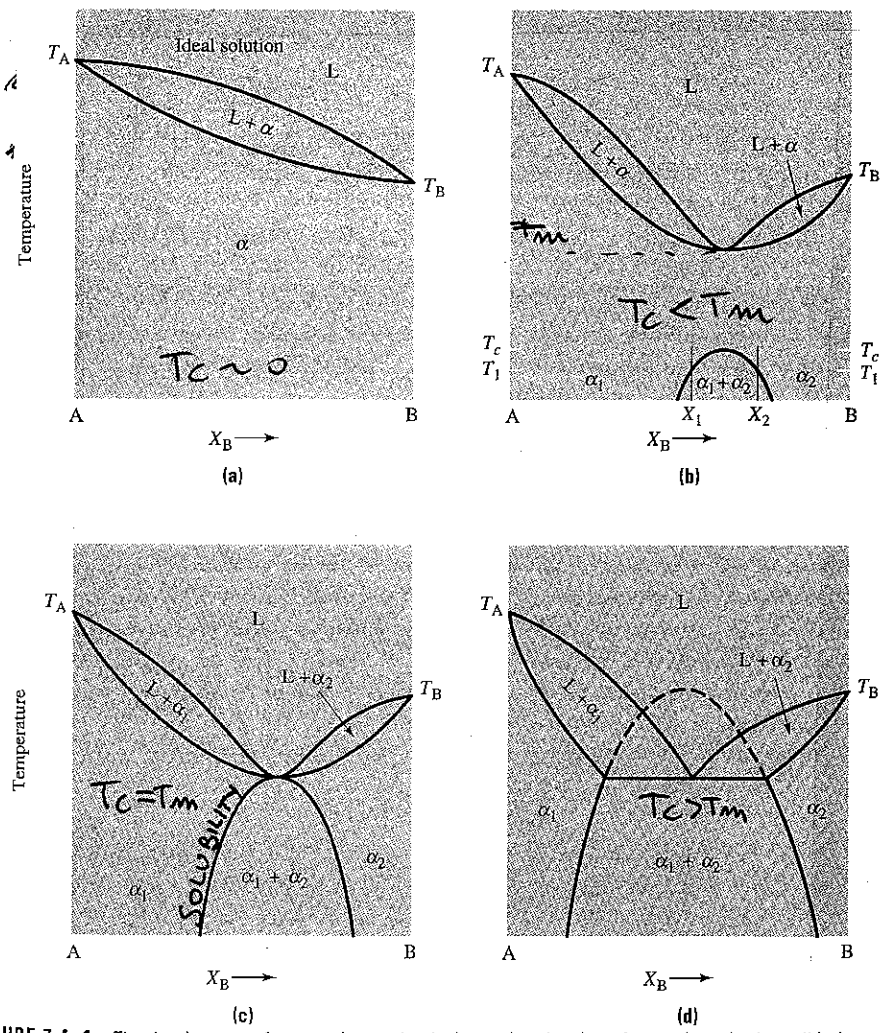



**FIGURE 7.4–1** The development of a eutectic reaction by increasing the clustering tendency in the solid phase: (a) the diagram for an ideal system, and (b–d) increasing clustering tendency in the solid phase.

↓

Like oil and water + sugar at low temperature

Above $T_c$
COMPLETE SOLUBITITY

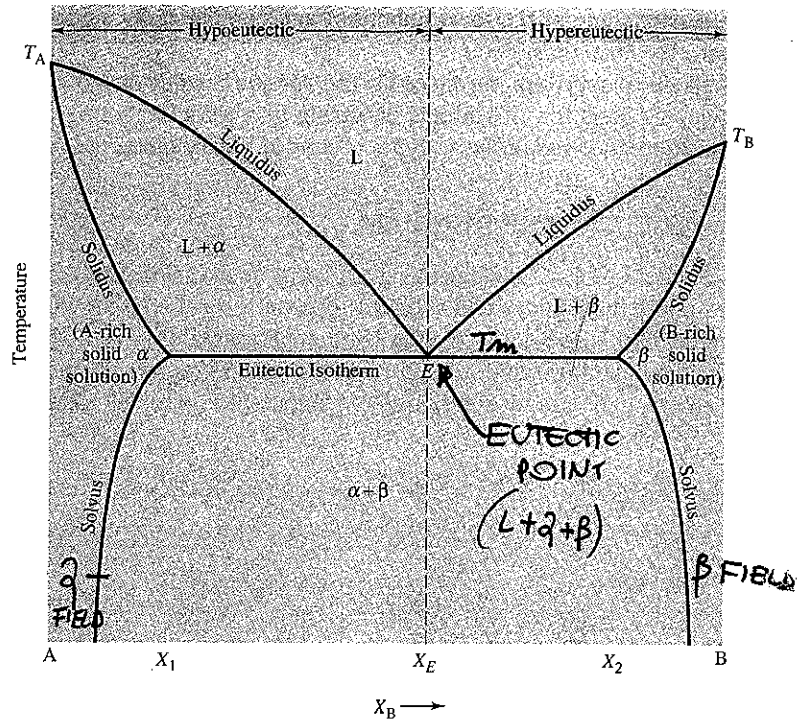
UNDER $T_c$
PARTIAL SOLUBILITY

A with B with Sol B in A
&
B with A with Sol A in B

High temp MIXING

low temp Separation water with little alcohol + solute + alcohol with little water solute

PE 22




IE 7.4–2 A binary eutectic phase diagram and the associated terms used to describe regions of a eutectic system.

SOLVUS = max solubility of a spec specie in the other.

EUTECTIC POINT

Coexistence of 3 phases

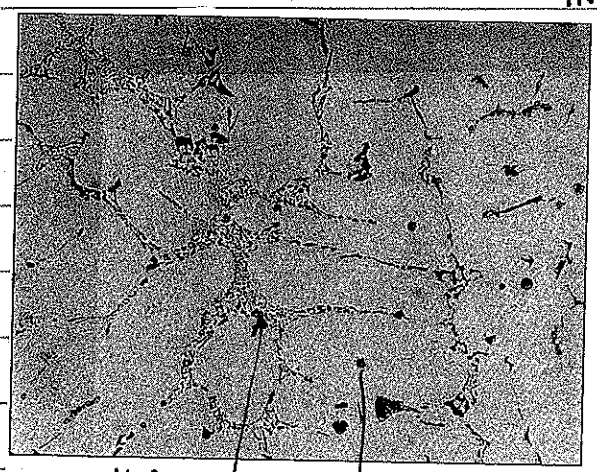
$\Rightarrow F = C - P + 2$

$2 - 3 + 1$ (1 because P is fixed)

$F = 0$

INVARIANT ← Eutectic point

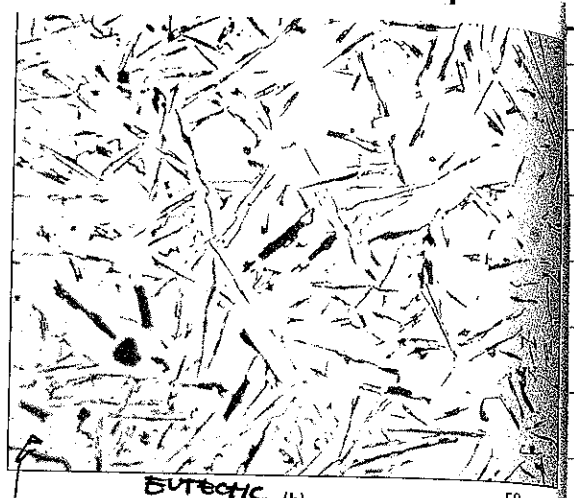
SOLVUS




HYPO EUTECTIC

Al Rich

EUTECTIC (Al+Si)




ALLEUTECTIC

EUTECTIC

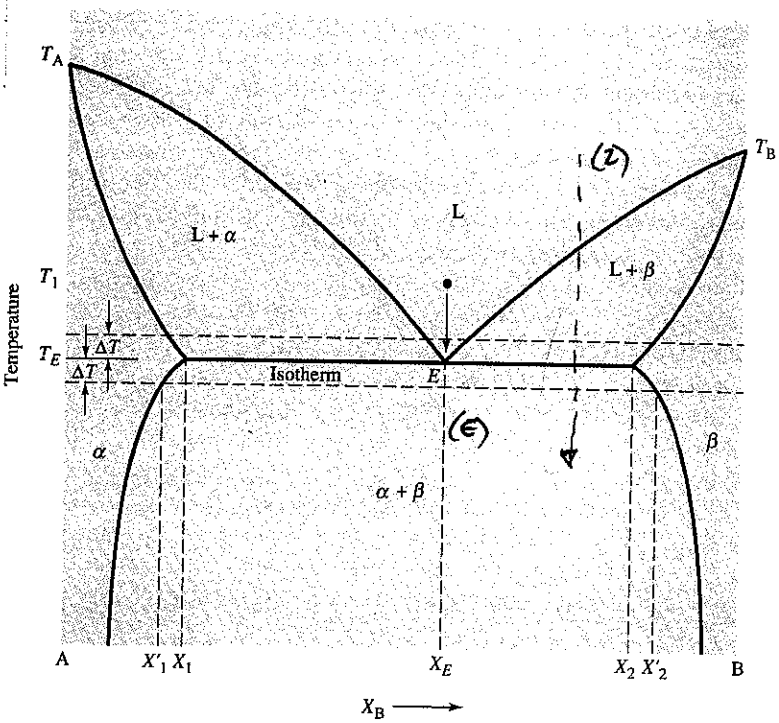
Si


**FIGURE 7.4–7**
Representative microstructures of Al-Si alloys. **(a)** The white areas are primary Al dendrites, and the dark areas are the eutectic constituent comprised of Al + Si. **(b)** Only the eutectic constituent is seen. **(c)** Primary Si is seen as blocky particles. The dark needles and light areas are the eutectic constituent. (*Courtesy of Ralph Napolitano.*)

PE23

# MELTING OF AN EUTECTIC ALLOY

go down at $X_E$ concentration through the T point



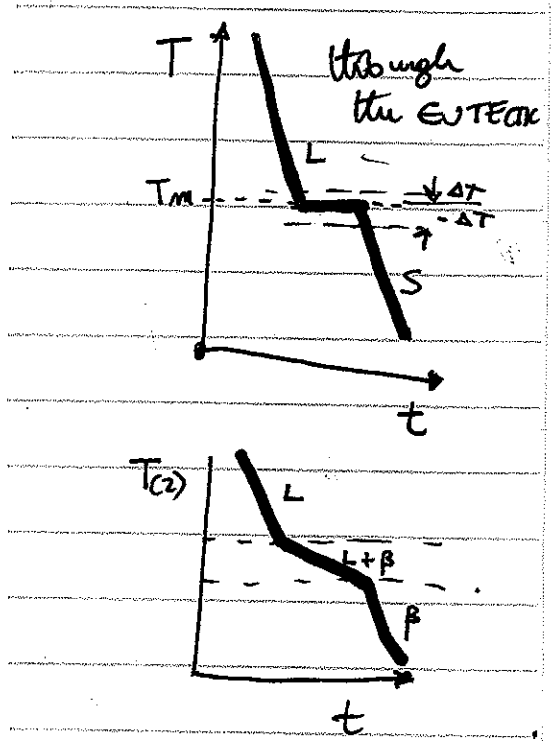




**FIGURE 7.4–3** A binary eutectic equilibrium phase diagram showing the changes in composition of the phases present as the temperature is changed by an amount $\Delta T$ above and below the eutectic isotherm.

note (ϵ) $L \rightleftharpoons \alpha + \beta$

at EUTECTIC POINT
very nice if ΔT ↑ all Liquid!
if ΔT ↓ all solid!

EUTECTIC $X = X_E$

$L^{X_E} \rightleftharpoons \alpha^{X_1} + \beta^{X_2}$

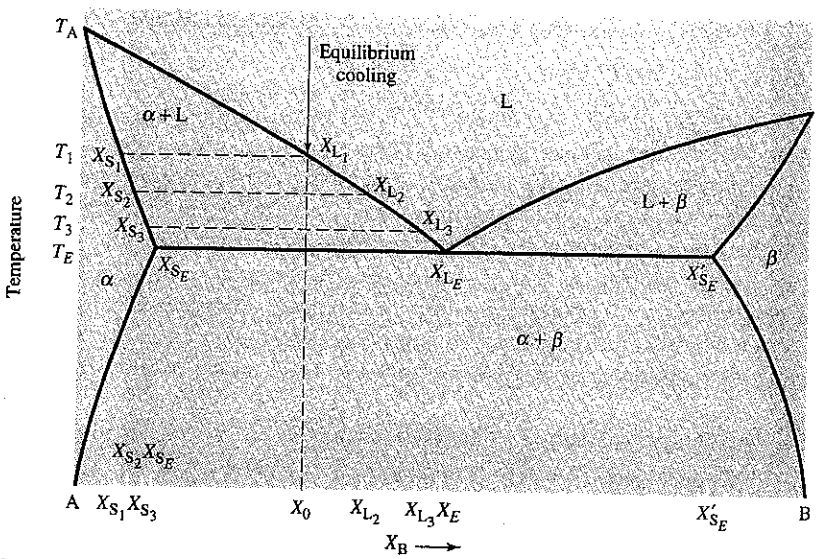



**FIGURE 7.4–4** Equilibrium solidification of an off-eutectic alloy of composition $X_0$.

OFF EUTECTIC $(X = X_0)$

@ $T_1$ $L^{X_0} \rightleftharpoons L^{X_0} + \alpha^{X_{S_1}}$

@ $T_2$ $\alpha^{X_{S_2}} + L^{X_{L_2}}$

@ $T_m$ $\alpha^{X_{S_E}}$ + NEXT PAGE

PE 24

# SOLIDIFICATION OF AN EUTECTIC ALLOY BUT OFF-EUTECTIC COMPOSITION

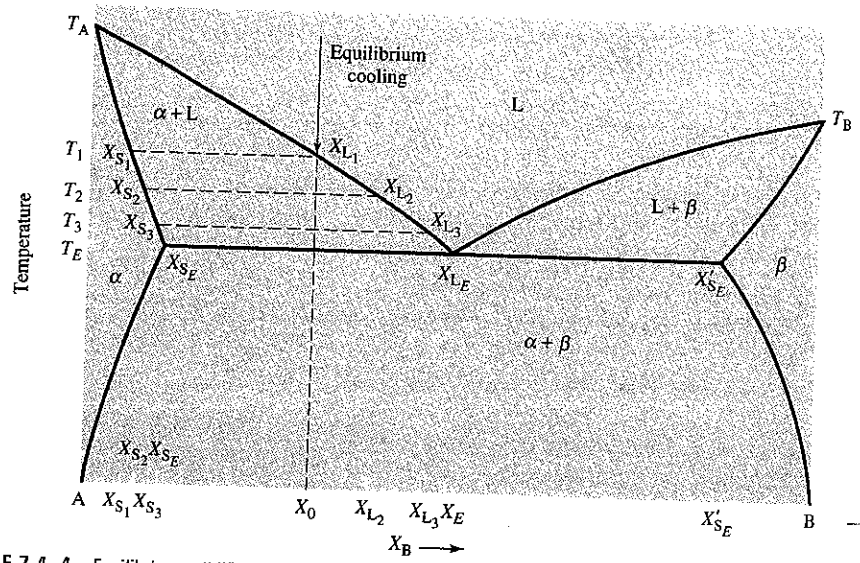



**FIGURE 7.4–4** Equilibrium solidification of an off-eutectic alloy of composition $X_0$.

@ $T_1$ $\quad L(X_{L_1}) \longleftrightarrow \alpha(X_{S_1}) + L(X_{L_1})$ $\quad f_{S_1} = \dfrac{X_{L_1} - X_0}{X_{L_1} - X_{S_1}}$ and $f_{L_1} = \dfrac{X_0 - X_{S_1}}{X_{L_1} - X_{S_1}}$

$f_{S_1}$ $\quad f_{L_1}$

@ $T_2$ $\quad \alpha(X_{S_2}) + L(X_{L_2})$ $\quad f_{S_2} = \dfrac{X_{L_2} - X_0}{X_{L_2} - X_{S_2}}$ and $f_{L_2} = \dfrac{X_0 - X_{S_2}}{X_{L_2} - X_{S_2}}$

$f_{S_2}$ $\quad f_{L_2}$

in $T_E \gtrsim T_E$

@ $T_M = T_E^{(+)}$ $\quad \alpha(X_{SE}) + L(X_{LE})$ $\quad f_{SE} = \dfrac{X_{LE} - X_0}{X_{LE} - X_{SE}}$ and $f_{LE} = \dfrac{X_0 - X_{SE}}{X_{LE} - X_{SE}}$

$T_M = T_E^{(-)}$ $\quad \alpha(X_{SE}) + \beta(X'_{SE})$ } 3 PHASES

$\alpha$ $\quad L$ $\quad X_0$ $\quad S(\alpha)$ $\quad L$ $\Rightarrow$ fractions
$X_{SE}$ $\quad$ NORM $\quad X_{LE}$

BUT A LOT of $\alpha$ & $\beta$ FORM SIMULTANEOUSLY in $T \lesssim T_E$ (IF IT HAS TIME TO REARRANGE)

in the same way fractions!

$S(\beta)$ $\quad X_{SE}$ $\quad X_0$ $\quad S(\alpha)$ $\quad X'_{SE}\beta$
$\alpha$ $\quad$ NORM

$f_{S_\alpha} = \dfrac{X'_{SE} - X_0}{X'_{SE} - X_{SE}}$ $\quad f_{S_\beta} = \dfrac{X_0 - X_{SE}}{X'_{SE} - X_{SE}}$ !!

PE 25

AT EUTECTIC POINT, a bit of $\alpha$ and $\beta$ form SIMULTANEOUSLY, and their MORPHOLOGY IS DIFFERENT FROM THE PRIMARY $\alpha$ and $\beta$! (IT'S BECAUSE OF THE SPEED (T(t)) ~~THE MORPHOLOGY~~ IT'S CABLED

$\Rightarrow$ therefore below EUTECTIC POINT

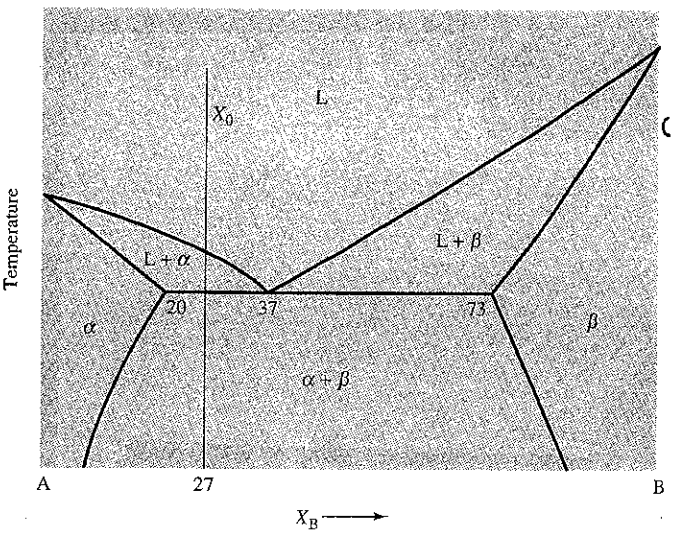
EUTECTIC ($\alpha+\beta$) vs PRIMARY

the ALLOY IS A MIXTURE of $\alpha$ + EUTECTIC ($\alpha+\beta$)

Note that for any alloy with composition in the range $X_{\alpha E} < X_0 < X'_{\alpha E}$, at the eutectic temperature liquid of composition $X_{LE}$ will transform to $\alpha$ and $\beta$ of compositions $X_{\alpha E}$ and $X'_{\alpha E}$, and that the relative amounts of $\alpha$ and $\beta$ formed from this liquid will be constant. In fact, this is what makes the eutectic reaction invariant.

UNLESS you go superslow, you always get EUTECTIC ($\alpha+\beta$)

## EXAMPLE




C

mposition 0.27 B. Calculate the following quantities:

*a.* The fraction of primary solid that forms under equilibrium cooling at the eutectic temperature.

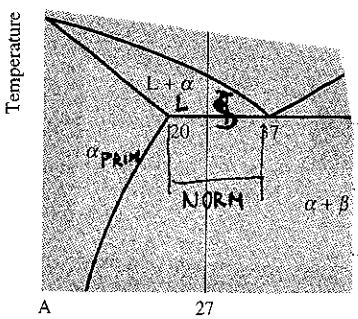
*b.* The fraction of liquid with the eutectic composition that will transform to two solid phases below the eutectic isotherm.

*c.* The amount of $\alpha$ and $\beta$ that will form from the liquid just below the eutectic isotherm.

*d.* The total amount of $\alpha$ phase in the alloy at a temperature just below the eutectic temperature.

a)

*a.* The fraction of primary solid that forms under equilibrium cooling at the eutectic temperature.




$$f_\alpha^P = \frac{X_L - X_0}{X_L - X_\alpha} = \frac{37 - 27}{37 - 20} = 0.588$$

(S over the numerator; NORM under the denominator)

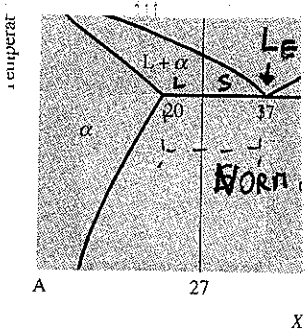
THIS IS $\alpha$-PRIMARY

$\alpha$ primary for $X_{SE} = 20\%$

PE 26

b) *b.* The fraction of liquid with the eutectic composition that will transform to two solid phases below the eutectic isotherm.

is the one at Liquid just before solidification.



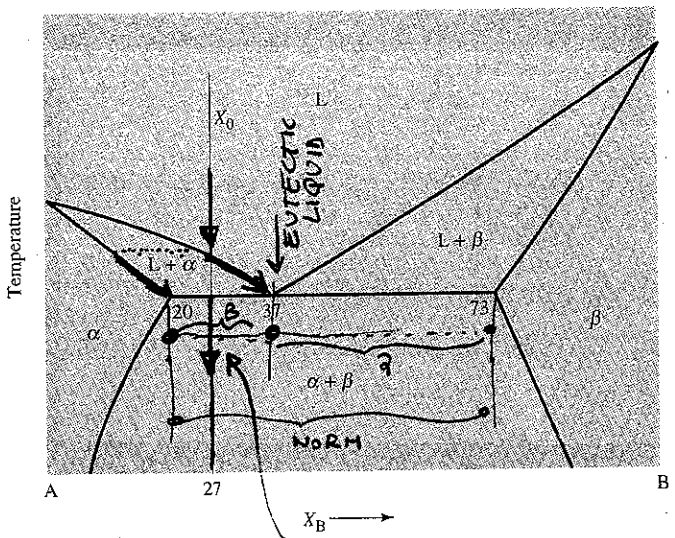

$$f_L^{eut} = \frac{X_0 - X_\alpha}{X_L - X_\alpha} = \frac{27 - 20}{37 - 20} = 0.412$$

NORM

$L_{EUT}$ has $X_{LE} = 37\%$

$= 1 - f_\beta^{Prim.}$

c) *c.* The amount of $\alpha$ and $\beta$ that will form from the liquid just below the eutectic isotherm.




Liquid at $T_E$ has composition $X_{LE} = 37\%$ (EUT. LIQUID just below the EUTECTIC POINT it becomes SOLID EUT SOLID $\alpha+\beta$ with $f_\alpha, f_\beta$

$$f_\alpha = \frac{X_\beta - X_L^{eut}}{X_\beta - X_\alpha} = \frac{73 - 37}{73 - 20} = 0.679$$

$$f_\beta = \frac{X_L^{eut} - X_\alpha}{X_\beta - X_\alpha} = \frac{37 - 20}{73 - 20} = 0.321$$

⇒ also here I HAVE $q^P$ + EUT $(\alpha+\beta)$

(a) $f_q^P = 0.588$

(b) $f_L^E = f_S^E = 0.412$

$f_q^P + f_q^{EUT} + f_\beta^{EUT} = f_q^{TOT} + f_\beta^{TOT}$

$f_q^P = 0.588$

$f_L^E * f_q = 0.412 * 0.679 = 0.280$

$f_L^E * f_\beta = 0.412 * 0.321 = 0.132$

⇓

ch which

$f_q = 0.679$

$f_\beta = 0.321$

PE27

d) *d.* The total amount of $\alpha$ phase in the alloy at a temperature just below the eutectic temperature.

$f_2^{TOT} = f_2^P + f_2^{EUT}$

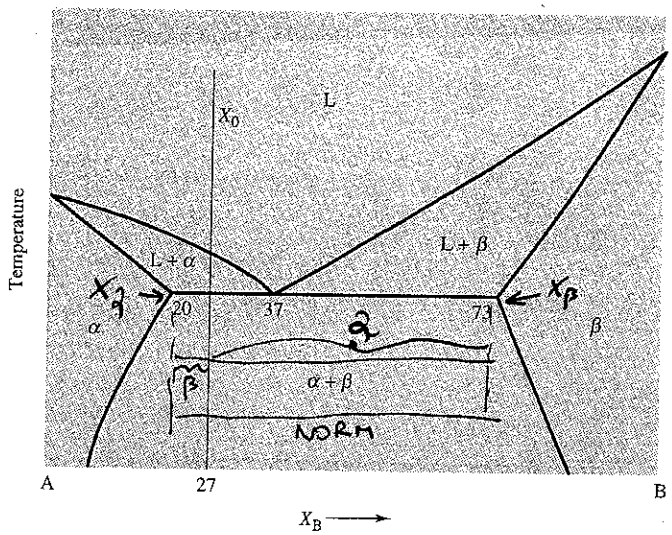
OR $1 - f_\beta^{EUT}$

OR

$$f_\alpha^{total} = f_\alpha^P + f_\alpha^{eut} = 0.588 + 0.280 = 0.868$$

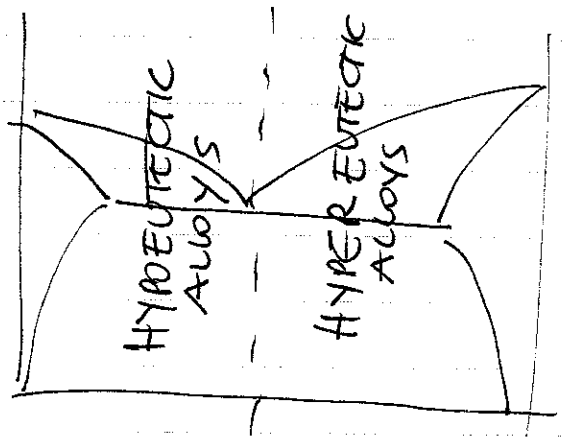
Alternatively, since the microstructure is composed of just two phases, $\alpha + \beta$, the total fraction of $\alpha$ must be given by:

$$f_\alpha^{total} = 1 - f_\beta^{eut} = 1 - 0.132 = 0.868$$




$$f_2 = \frac{X_\beta - X_0}{X_\beta - X_2}$$

$$f_\alpha^{total} = \frac{X_\beta - X_0}{X_\beta - X_\alpha} = \frac{73 - 27}{73 - 20} = 0.868$$




PE-28

# ALUMINUM- SILICON (CHIPS)

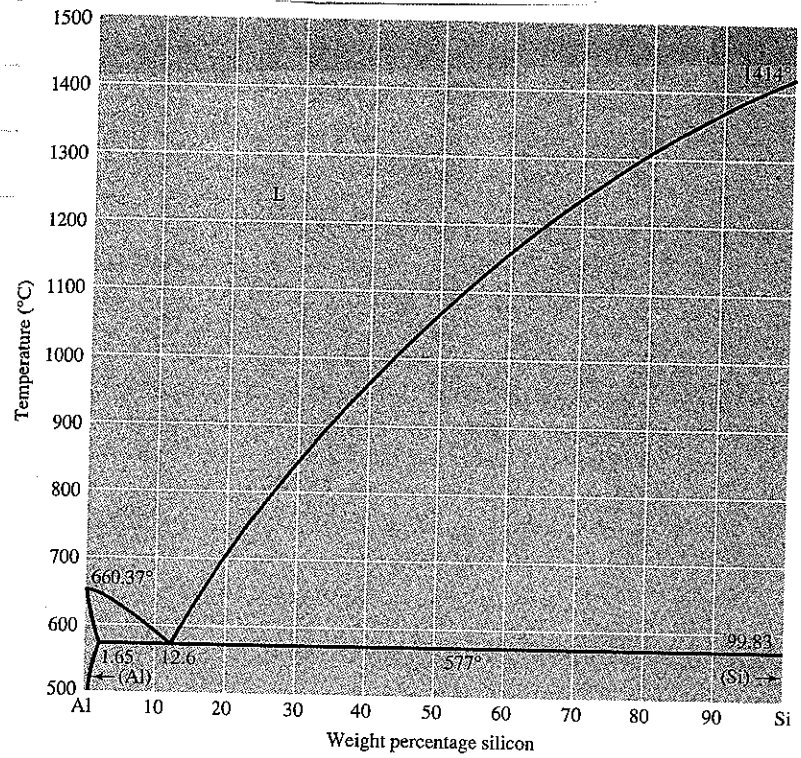



**FIGURE 7.4–6**
The Al-Si eutectic phase diagram. (*Source: F. Shunk, Constitution of Binary Alloys, McGraw-Hill. Reproduced with permission of McGraw-Hill.*)

(CARS (PISTONS)

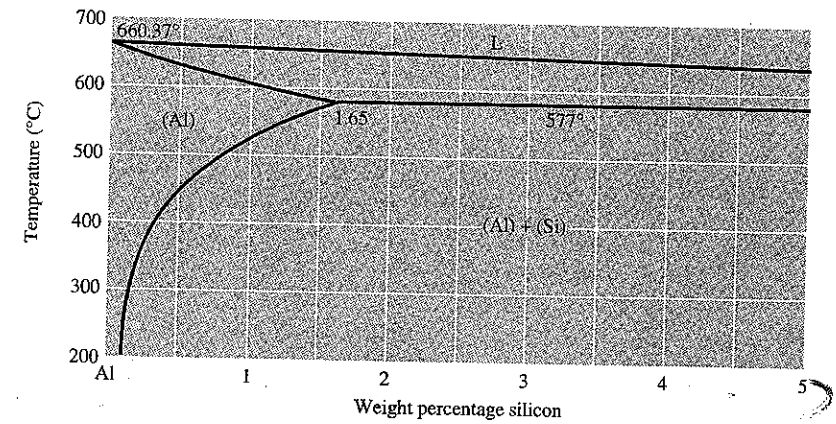
(HARD, Si⇒ Wear Resistance)

look at Page PE23

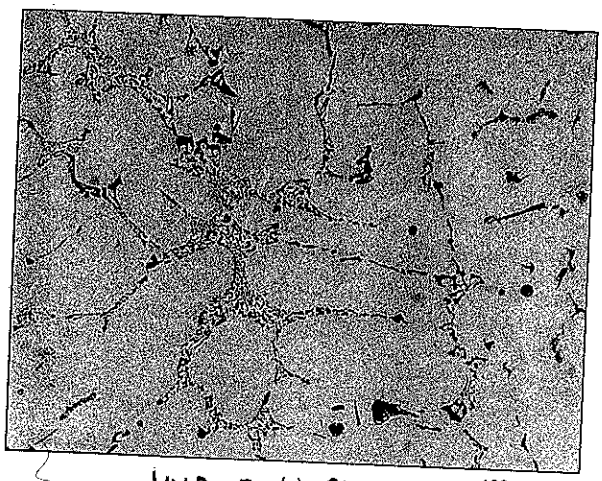
~~BTRO~~

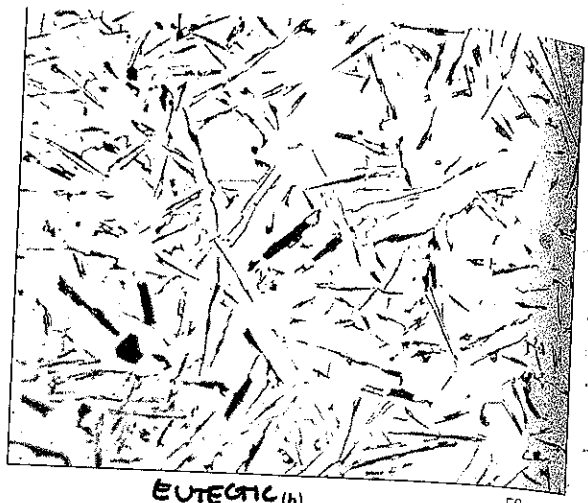
(CLUSTERING)= TENDENCE

Al = LIGHT




PE 29



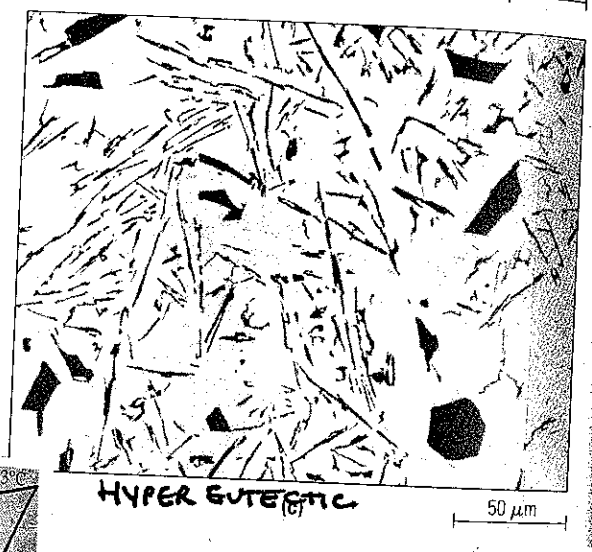
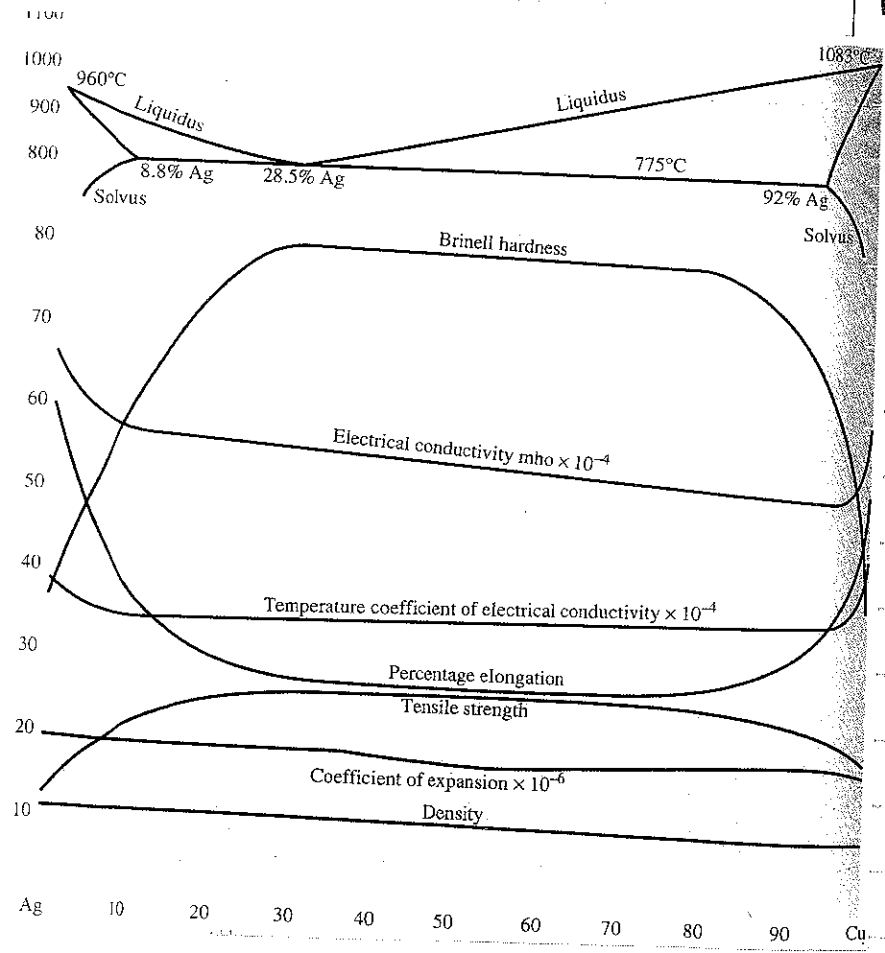




**FIGURE 7.4–7**

Representative microstructures of Al-Si alloys. **(a)** The white areas are primary Al dendrites, and the dark areas are the eutectic constituent comprised of Al + Si. **(b)** Only the eutectic constituent is seen. **(c)** Primary Si is seen as blocky particles. The dark needles and light areas are the eutectic constituent. *(Courtesy of Ralph Napolitano.)*




← PROPERTIES

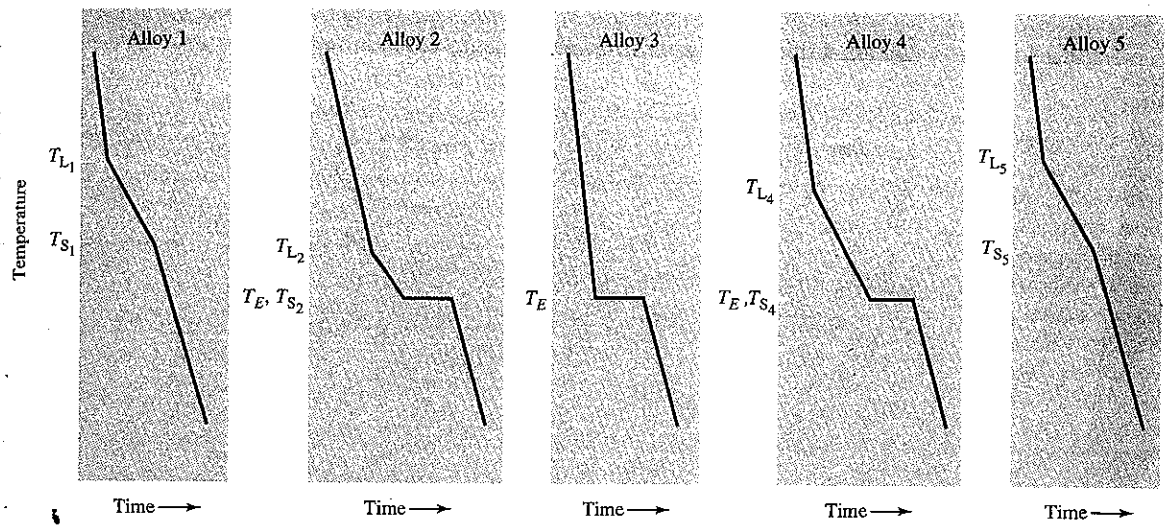
VS

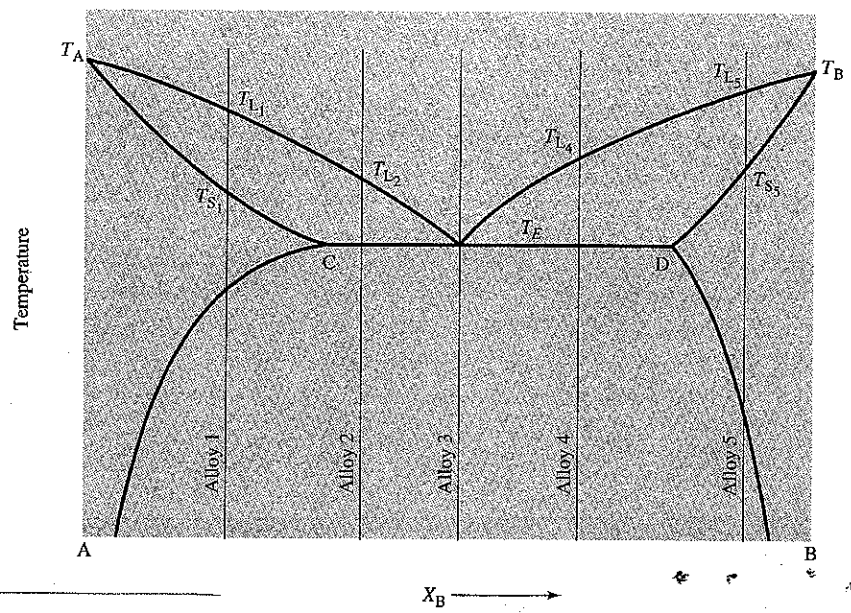
CONCENTRATION

PE 30

# HOW TO MEASURE

melt & watch T(t) behaviour




Temperature PROFILES (c)

Properties PROFILE (c)

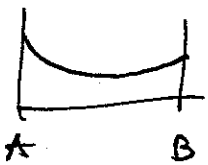
PE31

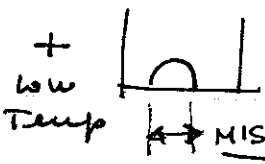
# TWO EUTECTICS

A likes A more than B $\Rightarrow E_{AB} > \frac{1}{2}(E_{AA}+E_{AB}) \Rightarrow$ CLUSTERING TEND

$\Rightarrow$ WEAKER SOLID SOLUTION

$\Rightarrow$ STRONGER LIQUID



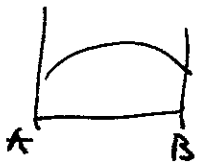




$\Rightarrow$ Eutectic

A likes B more than A $\Rightarrow E_{AB} < \frac{1}{2}(E_{AA}+E_{AB}) \Rightarrow$ ORDERING TEND

$\Rightarrow$ STRONGER SOLID SOLUTION

$\Rightarrow$ WEAKER LIQUID

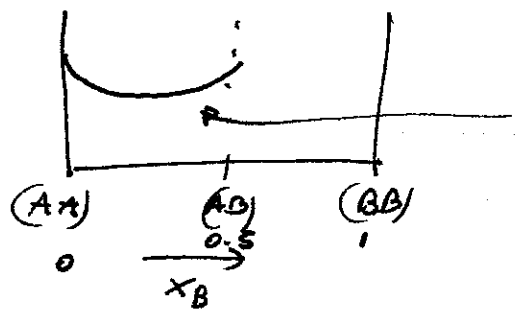



TAKE 2 ATOMS (AA), (AB), (BB)

(AA) likes (AA) more than (AB) (depends from structures!)

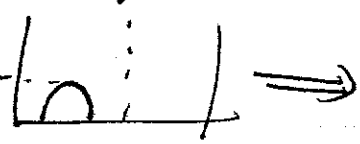
$\Rightarrow E_{AA-AB} > \frac{1}{2}(E_{AA-AA} + E_{AA-BB})$

$\Rightarrow$

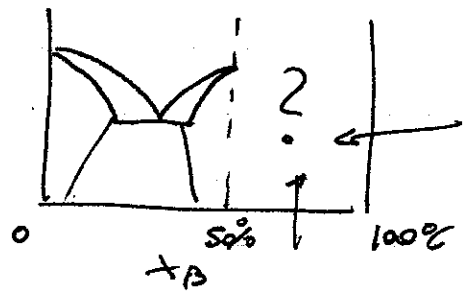



STOPS AT 50% here or elsewhere

IF low temperature IMMISCIBILITY of AA & AB (NO SOLID SOLUTION) $\Rightarrow$



the system can form an eutectic between 0 & 50%




may be another eutectic between AB & BB

Rule: between two strong chemical compounds you can form an eutectic

(CAN = MAY ≠ MUST = HAS TO).

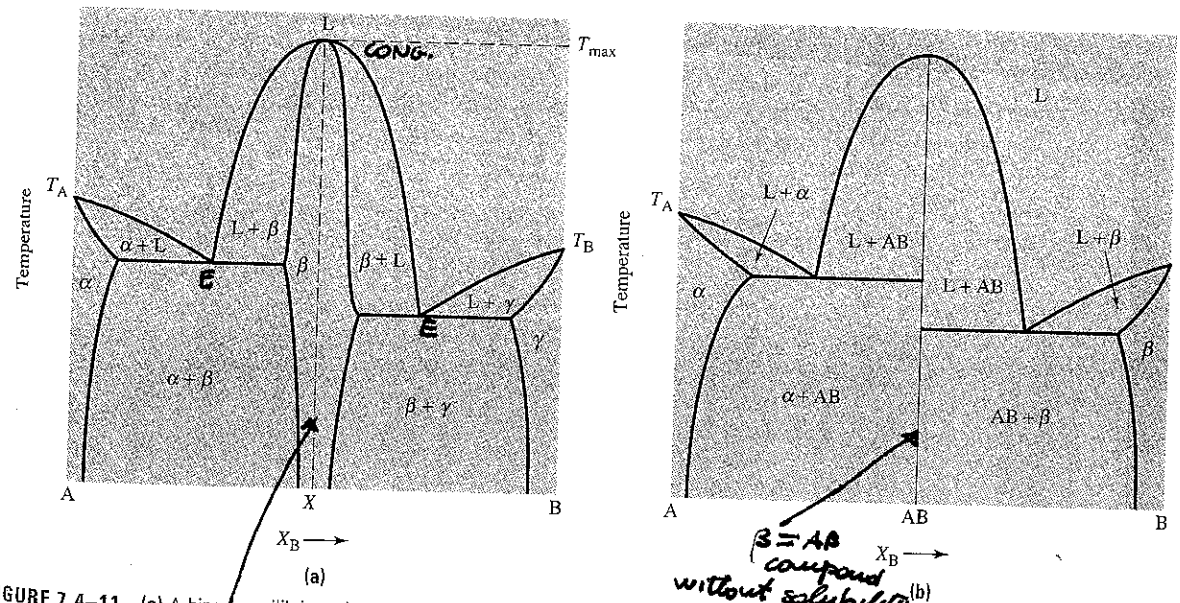
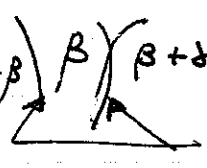



**FIGURE 7.4–11** **(a)** A binary equilibrium phase diagram containing two eutectic reactions illustrating solid solution ranges, an intermediate phase $\beta$, and a congruent melting reaction. **(b)** When the solubility of the intermediate phase becomes limited, the line compound AB results.

intermediate phase β

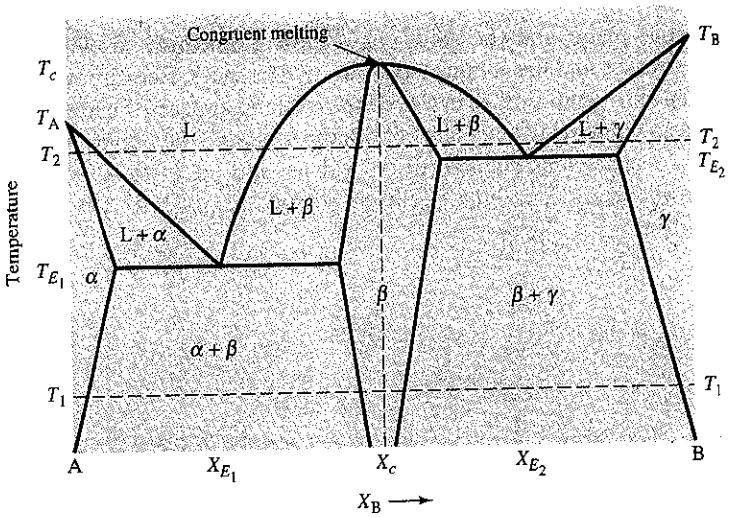



Solubilities of β in α & γ

PE 33

# EXAMPLES

(changing T)



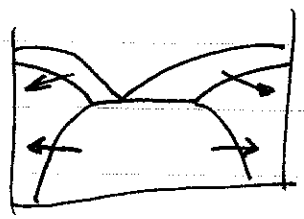

Reactions @ the invariant points (00)

1. Eutectic reaction at $T_{E_1}$ and $X_{E_1}$: $L \leftrightarrows \alpha + \beta$
2. Eutectic reaction at $T_{E_2}$ and $X_{E_2}$: $L \leftrightarrows \beta + \gamma$
3. Congruent melting at $T_c$ and $X_c$: $L \leftrightarrows \beta$

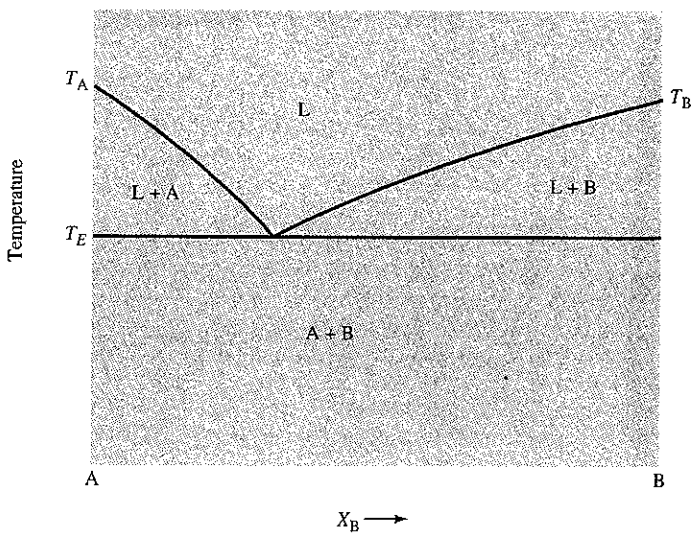
only

only

# IF NO SOLUBILITIES



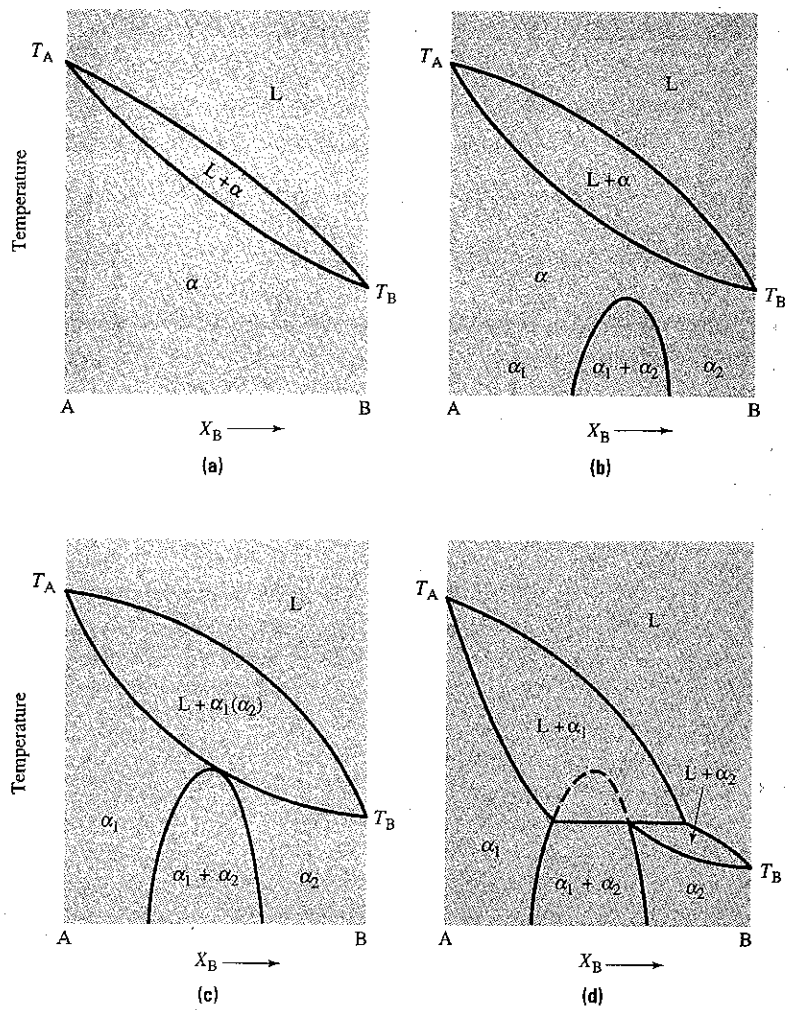
A Hates mixing with B but only in the liquid phase they do, because the higher entropy of the Liquid

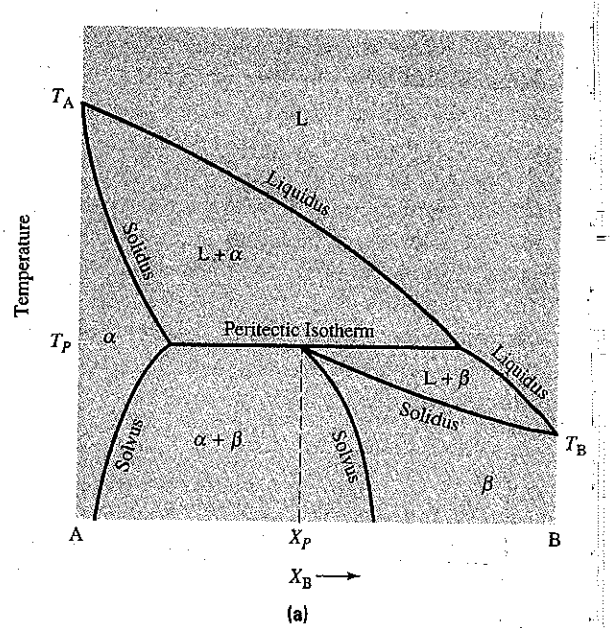



PE34

# PERITECTIC SYSTEMS

1) ~~Both~~ A likes A more than B (SOLID CLUSTERING) ~~at~~ low temperature (MISCIBILITY GAP)
2) melting point very different
3) A likes A more than B also at high temperature (CLUSTERING OF LIQUIDS) ⇒ LENS BECOME WIDER

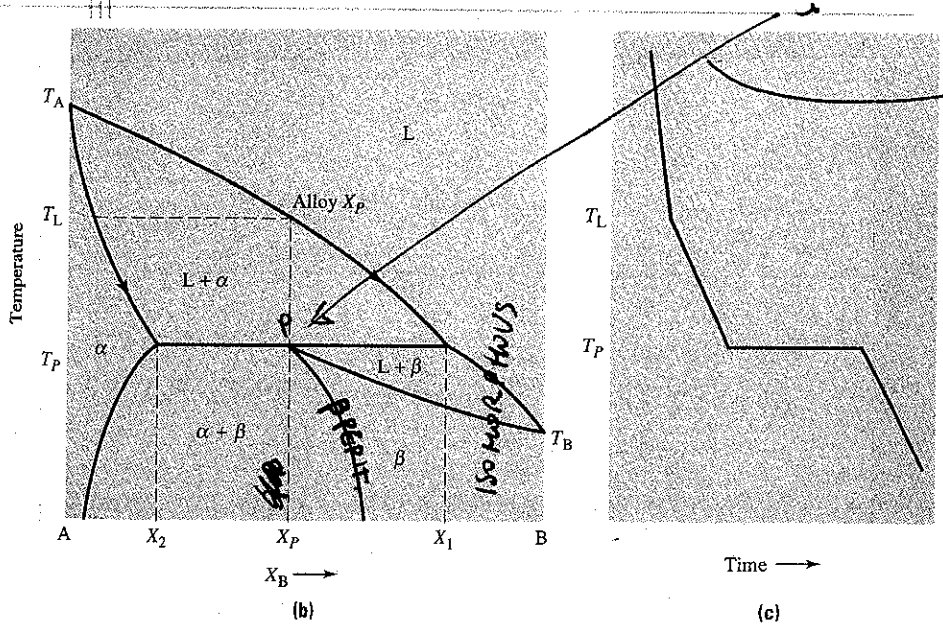




PE 35

**FIGURE 7.5–1** Development of a peritectic system by increasing the clustering tendencies of the solid and liquid phases. The clustering tendency for the solid is greater than that of the liquid. (*Source: Adapted from Albert Prince,*

at Peritectic point
INVARIANT
TRANSORMATION
$L+\beta \rightleftarrows \beta$
but $\pm\Delta T \Rightarrow$ produce $\beta$ !!

# TEMPERATURE BEHAVIOR OF PER.



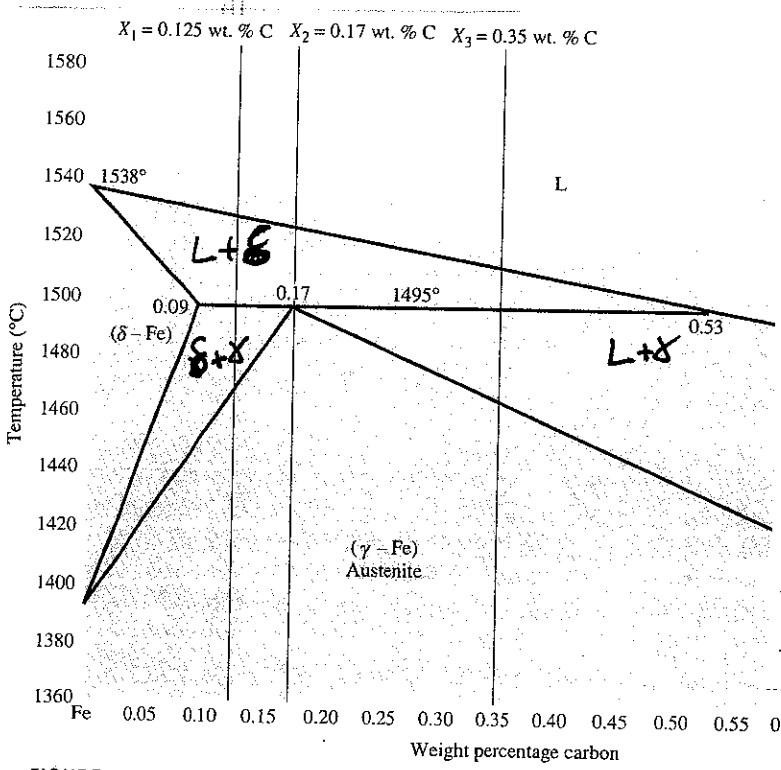

at Peritectic

$L + \alpha \rightleftharpoons \beta$

$\beta$ gets broken and changes concentration with T.

**FIGURE 7.5–2** **(a)** A binary peritectic phase diagram and the associated terms used to describe regions of a peritectic system, **(b)** a simple peritectic system showing the equilibrium cooling of an alloy whose composition is the peritectic composition $X_P$, and **(c)** the corresponding cooling curve for alloy $X_P$.

X in weight ⇒ f in weight




| | Above peritectic | Below peritectic |
|---|---|---|
| **Alloy 1** | $T = T_P + \varepsilon$ | $T = T_P - \varepsilon$ |
| $f_L$ | $\frac{0.125 - 0.09}{0.53 - 0.09} = 0.080$ | 0 |
| $f_\delta$ | $\frac{0.53 - 0.125}{0.53 - 0.09} = 0.920$ $\delta^{PRIM}$ | $\frac{0.17 - 0.125}{0.17 - 0.09} = 0.563$ |
| $f_\gamma$ | 0 | $\frac{0.125 - 0.09}{0.17 - 0.09} = 0.437$ $\gamma^{PER}$ |
| **Alloy 2** | | |
| $f_L$ | $\frac{0.17 - 0.09}{0.53 - 0.09} = 0.182$ | 0 |
| $f_\delta$ | $\frac{0.53 - 0.17}{0.53 - 0.09} = 0.818$ $\delta^{PRIM}$ | 0 $\delta^{PER}$ |
| $f_\gamma$ | 0 | 1.0 (single phase) |
| **Alloy 3** | | |
| $f_L$ | $\frac{0.35 - 0.09}{0.53 - 0.09} = 0.591$ | $\frac{0.35 - 0.17}{0.53 - 0.17} = 0.500$ |
| $f_\delta$ | $\frac{0.53 - 0.35}{0.53 - 0.09} = 0.409$ $\delta^{PRIM}$ | 0 $\gamma^{PER}$ |
| $f_\gamma$ | 0 | $\frac{0.53 - 0.35}{0.53 - 0.17} = 0.500$ |

$x_L = 12$
$x_\delta = 9$
$x_\gamma = 17$

$L + \delta \rightleftharpoons \gamma$

**FIGURE 7.5–3** A simple peritectic diagram showing three specific alloy compositions. Refer to Example 7.5–1 for a discussion of this phase diagram.

# MONOTECTIC PHASE DIAGRAM

like eutectic but for liquids!

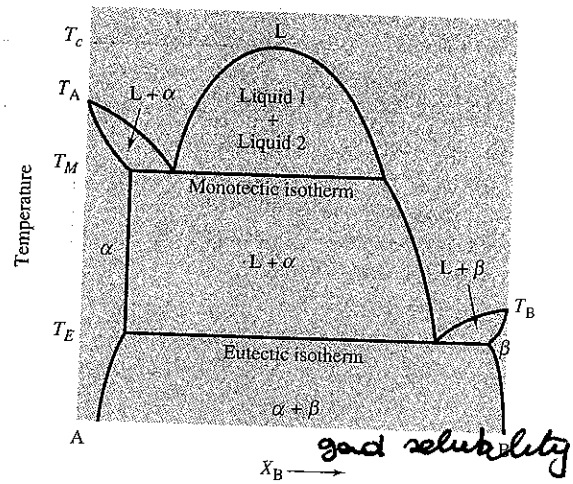
liquid A dissolves liquid B ⇒ almost mix

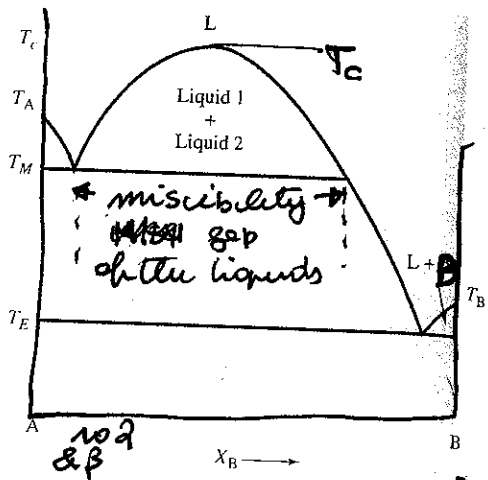
⇒ miscibility gap for liquids (region $L_1 + L_2$)

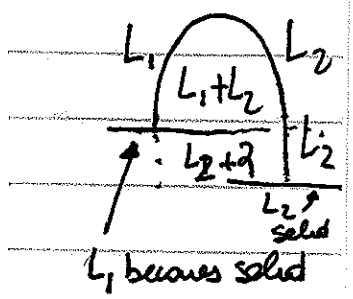
and results Liquid 1 & Liquid 2 outside.

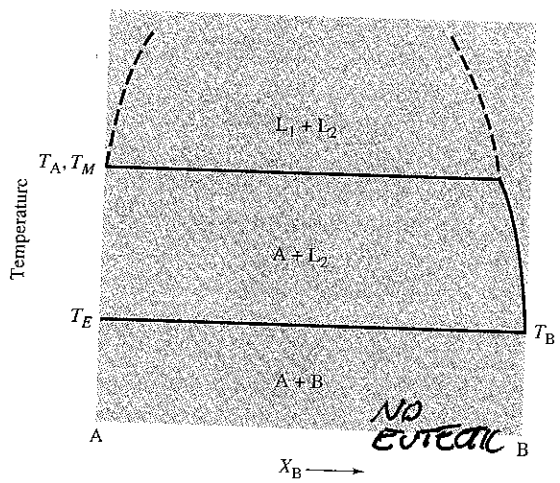
OIL + WATER.

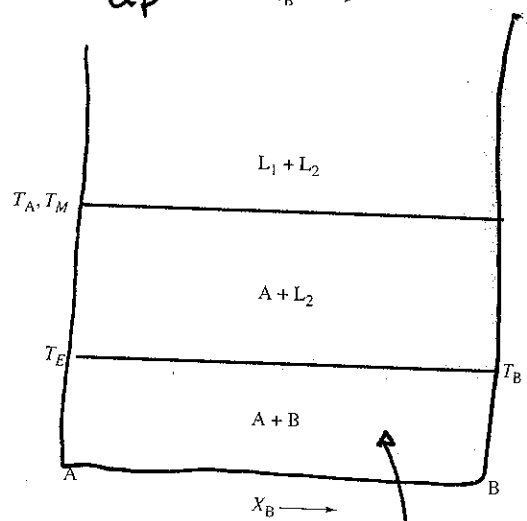
Mix only at high temp

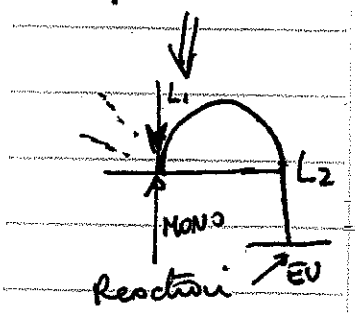


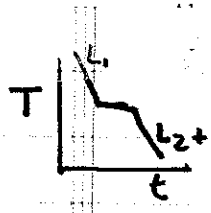




another invariant point!

**FIGURE 7.6–1** The limiting case of the monotectic reaction occurs when there is effectively no mutual solubility in either the liquid or solid phase.




⇒ β is not β PRIMITIVE but MONOTECTOID

SUMM:
EU $L \rightleftharpoons \alpha + \beta$
PER $L + \alpha \rightleftharpoons \beta$
MONO $L_1 \rightleftharpoons L_2 + \beta$
C. Melt $L \rightleftharpoons \alpha$

NO SOLUBILITY FOR SOLIDS & LIQUIDS!

C ≠ W

only way to MIXING is melting

3 phases

$F = C - P + 2$

$= 2 - 3 + 1$

$= 0$

OD point INVARIANT

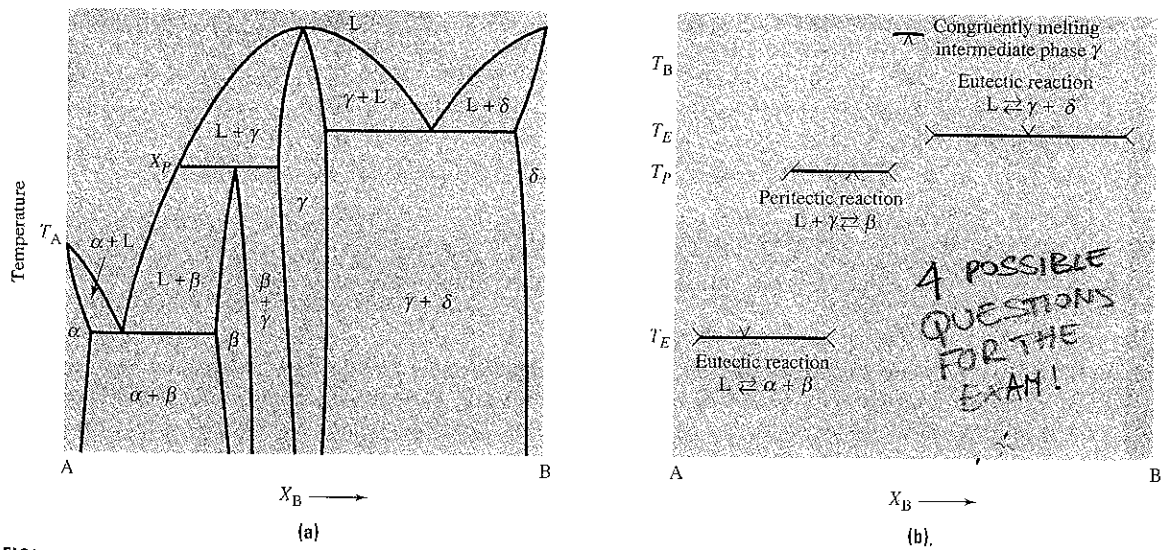
PE 37

# COMPLEX DIAGRAMS : diversity IS FUN!

1) for students everything is complex
2) for professors complex systems = many 2 phase regions & invariant points

Remember

- CONGRUENT MELTING — $L \rightleftharpoons \gamma$
- EUTECTIC POINT — $L \rightleftharpoons \gamma + \beta$ (eutectic)
- PERITECTIC POINT — $L + \gamma \rightleftharpoons \beta$ (peritectic)
- MONOTECTIC POINT — $L_1 \rightleftharpoons L_2 + \gamma$ (monotectic)




4 POSSIBLE QUESTIONS FOR THE EXAM!

PE38

**FIGURE 7.7–1** **(a)** Complex phase diagram containing a peritectic and two eutectic reactions, and **(b)** the invariant reactions in **(a)** emphasized along with their symbolic representations. When the $\beta$ phase is heated to the peritectic temperature, an incongruent melting reaction occurs at $T_P$, the peritectic temperature.

IDEA: BREAK PHASE DIAGRAMS IN "AS MANY PART AS POSSIBLE" ⇒ IT BECOMES EASIER

EXTRA TROUBLE:

- INCONGRUENT MELTING: $L + ? \rightleftharpoons \beta$

  In Liquid solidifies to a phase with different concentration? HOW IS THIS POSSIBLE?

  $L + ? \rightleftharpoons \beta$

  $x_L$ ↙ ? ↗ $x_\beta \neq x_L$ (? = something else)

  $L + 2 \rightleftharpoons \beta$ = like in peritectic

IF NO SOLUBILITIES ON intermediate phases

PHASES (BROAD CONCENTRATION) $\xrightarrow{\text{NO SOLUBILITIES}}$ COMPOUNDS

$\alpha, \beta, \gamma \ldots \Longrightarrow A, B, A_2B \ldots$

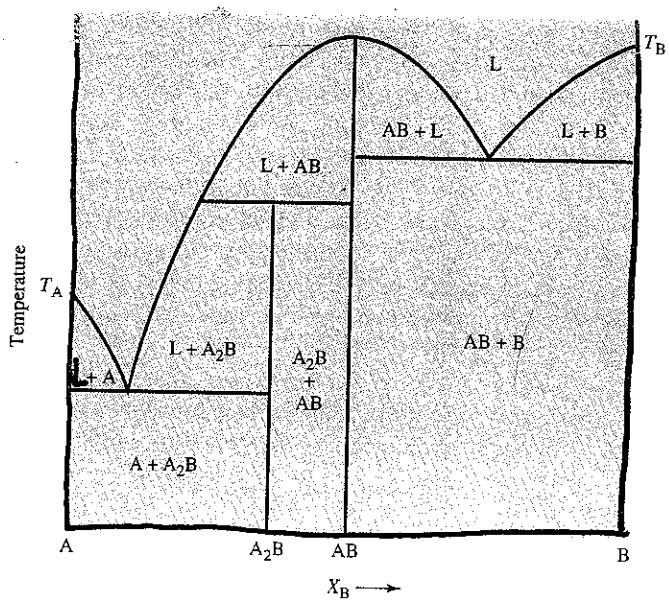



**FIGURE 7.7–2** A diagram similar to Figure 7.7–1, but the $\beta$ and $\gamma$ are seen as line compounds. The $\alpha$ and $\delta$ phases are terminal solid solutions with essentially no solubility. Thus, they are simply labeled A and B, corresponding to the pure components.

PE 39

# NICKEL-ALUMINUM

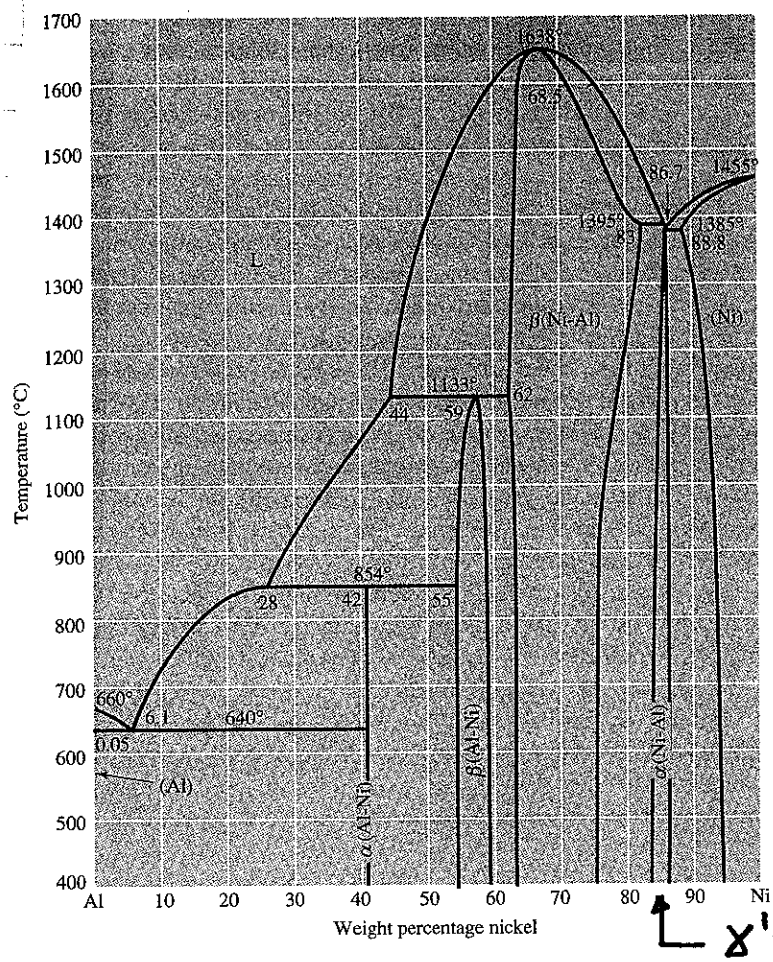



**FIGURE 7.7–3**
The Al-Ni binary phase diagram.

It is worth noting that $\alpha$(Ni-Al) is often called $\gamma'$ and is the basis of strengthening in Ni-base superalloys.

$\gamma'$ = FUNDAMENTAL IN STRENGTHENING OF NI-SUPERALLOYS

( PRECIPITATES OF $\gamma'$ FORM & AGLOMERATES THAT STOP DISLOCATION MOVEMENTS

BREAK PLASTICITY
KEEP ELASTICITY } NO DEFORMATION PERMANENT

SUPERALLOY!!

PE 40

# PHASE EQUILIBRA WITH SOL–SOL REACTION

LIQUID REACTION

$L \rightleftharpoons \alpha + \beta$ EUTECTIC

$L + \alpha \rightleftharpoons \beta$ PERITECTIC

$L_1 \rightleftharpoons L_2 + \alpha$ MONOTECTIC

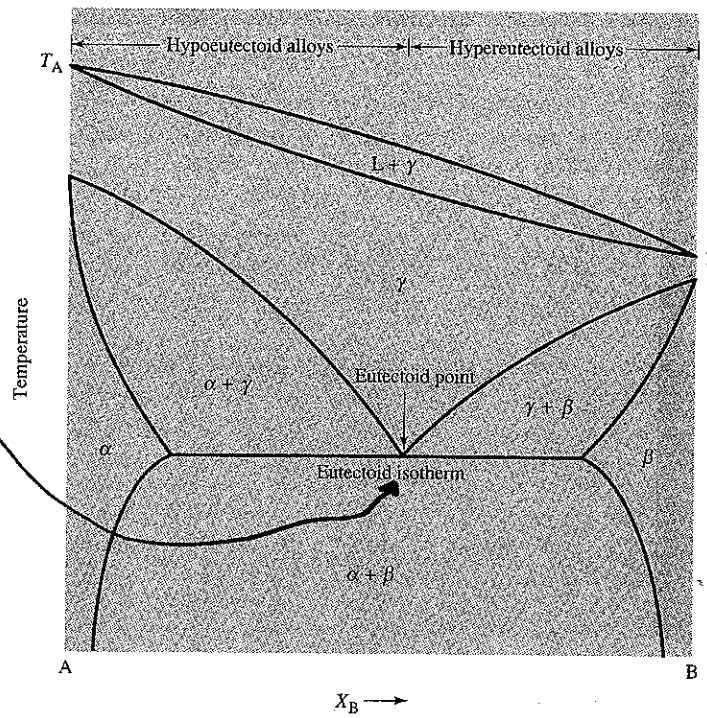
SUBSTITUTE L with a plain solid $\gamma$

$\gamma \rightleftharpoons \alpha + \beta$ EUTECTOID

$\gamma + \alpha \rightleftharpoons \beta$ PERITECTOID

$\gamma_1 \rightleftharpoons \gamma_2 + \beta$ MONOTECTOID

**FIGURE 7.8–1**
A general eutectoid equilibrium phase diagram with associated definitions.

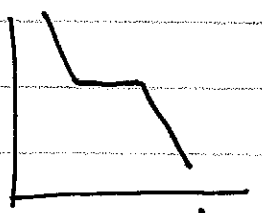



EUTECTOID SYSTEM

SOLID PH. decomposes in 2 SOLID PHASES

$\gamma \rightleftharpoons \alpha + \beta$

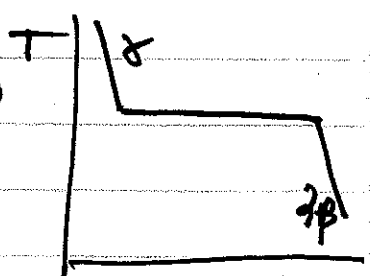
EUTECTIC




$L \rightleftharpoons \alpha + \beta$

Reactions are fast because diffusion in L is fast $\Rightarrow$ $\alpha, \beta$ low time to FORM & separate

EUTECTOID




$\gamma \rightleftharpoons \alpha + \beta$

Reaction are slow diffusion in solid is slow $\rightarrow$ $\alpha, \beta$ slowly growing!

diff is Faster along grain boundaries $\Rightarrow$ EUT. $\alpha, \beta$ growth FROM G.B.

PE41

# IRON - CARBON HAS EUTECTOID

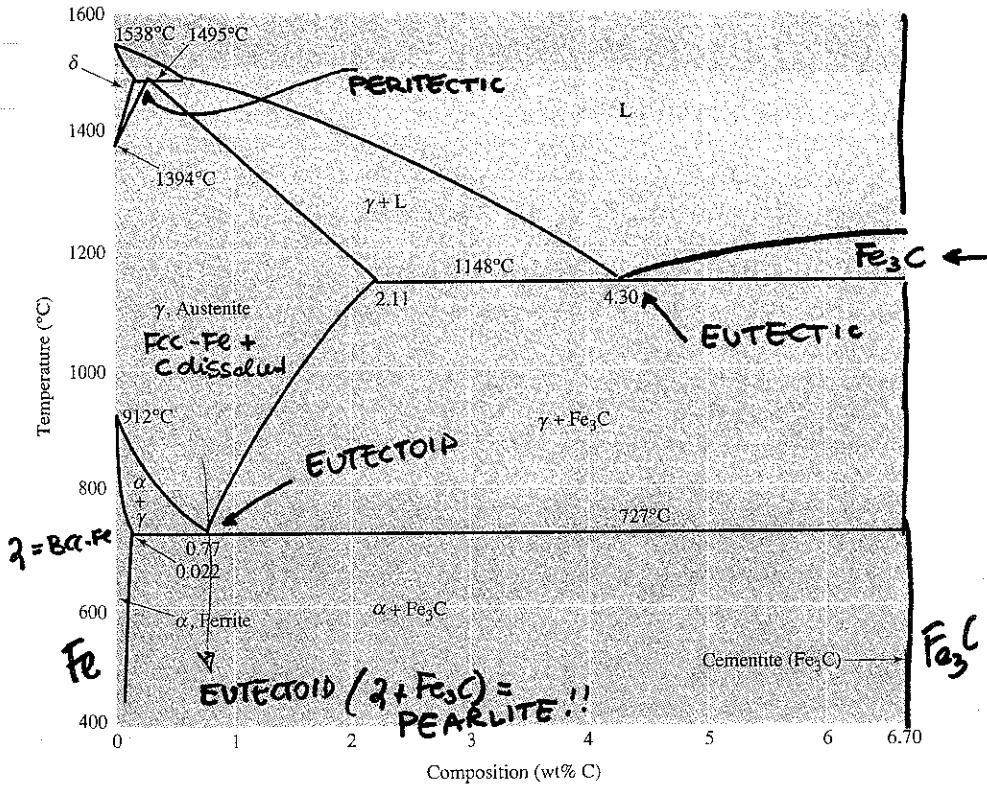



FIGURE 7.8–2 The Fe-$Fe_3C$ system with the important phase fields defined.

See: No solubility of Fe in $Fe_3C$

BOOK: TAKE γ (austenite) with 0.77% w of C & cool down

EUTECTOID @ 727 °C

$$\gamma \rightleftharpoons q^{PRIM} + \underbrace{(q + Fe_3C)}_{\text{Pearlite}}^{EUTECTOID}$$

γ: Austenite; q: Ferrite

SEE: solubility of C in γ (FCC-Fe) is bigger than in q (BCC-Fe)

WHY?

↳ as long as you have γ (with > 0.022 % w of C ⇒ you get pearlite)

IN PRACTICAL WORDS:

WE HAVE PEARLITE ALL OVER THE PLACE

PE42

EUTECTOID ($\alpha + Fe_3C$) = PEARLITE

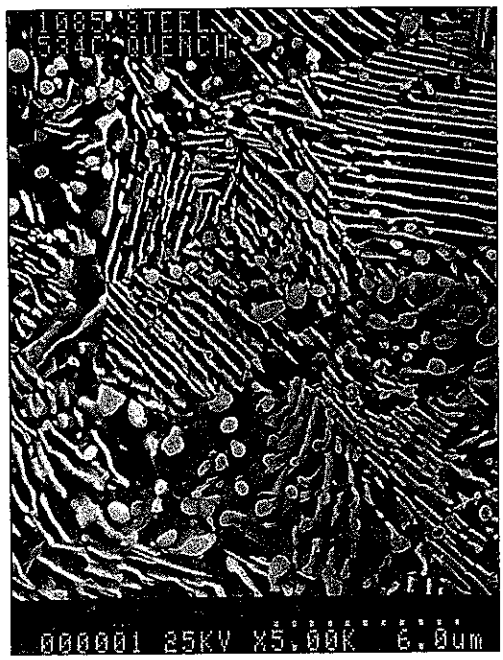



**FIGURE 7.8–3** Structure of the eutectoid composition 0.77 wt. % C steel. The eutectoid constituent, called pearlite, has a lamellar (layered) morphology consisting of alternating plates of $\alpha$ Fe (light areas) and $Fe_3C$ (dark areas).

COPPER-ALUMINUM.

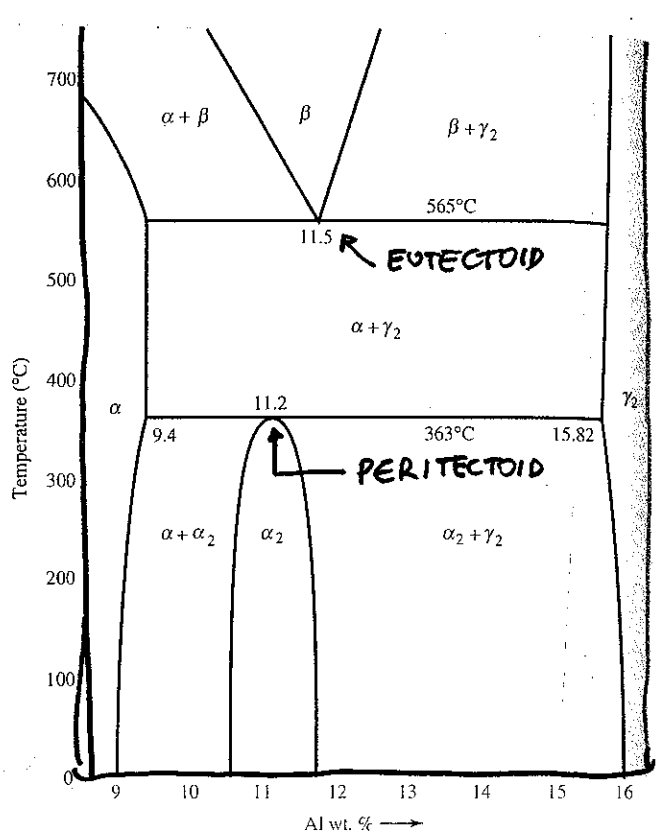



**FIGURE 7** The copper-rich side of the Cu-Al system shows a peritectoid reaction in the approximate temperature range of 300–400°C. Symbolically the reaction is written $\alpha + \gamma_2 \rightleftarrows \alpha_2$. *(Source: Adapted from Albert Prince,* Alloy Phase Equilibria, *1966. Permission granted from Elsevier Science.)*

ZINC ALUM.

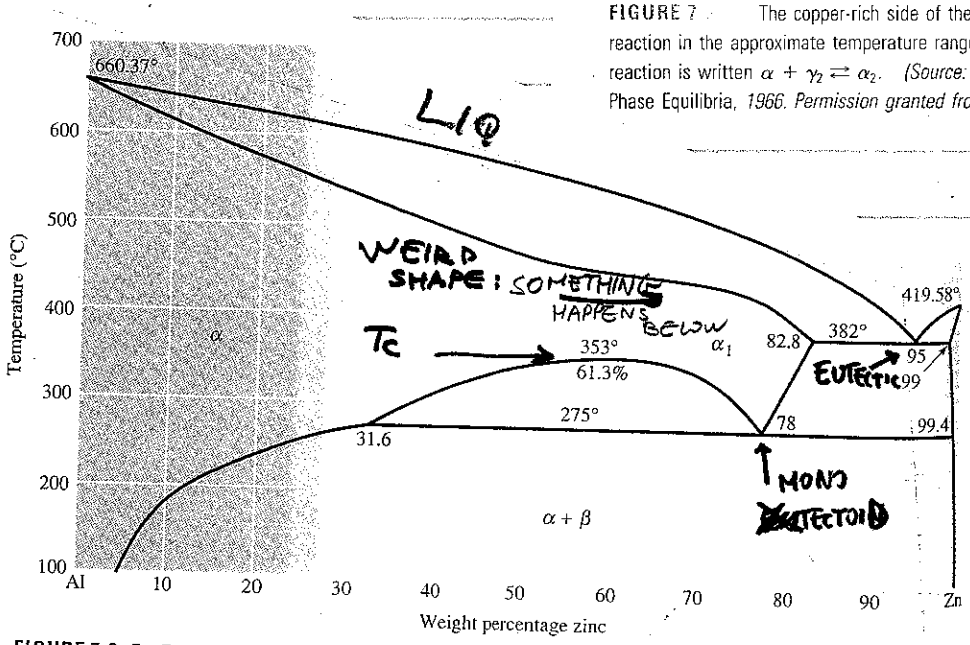



**FIGURE 7.8–5** The Al-Zn systems contain a monotectoid reaction at 275°C. Symbolically the reaction is $\alpha_1 \rightleftarrows \alpha + \beta$.

PE 43